Volume 7 NOVEMBER, 1936 Number 11

PHYSICS

A Journal of General and Applied Physics

An Application of Infrared Spectroscopy to Rubber Chemistry

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(Received August 3, 1936)

The applicability of infrared methods to some problems arising in the chemistry of rubber has been demonstrated. The spectra of isoprene, styrene, polymerized butadiene, and several types of rubber have been studied and certain variations in the 5.5μ–6.5μ regions are attributed to changes occurring during the processes of polymerization. The effects of vulcanization also appear in the spectra of the rubber samples. The methods of infrared analysis do not necessitate the use of solutions of rubber compounds in carbon tetrachloride or carbon disulphide as in the case of previous Raman work.

IN his recent article Barnes[1] has described some of the applications of infrared spectroscopy to problems involving the structure and effective binding forces of complicated organic molecules. The interpretations of the spectra of complex molecules are necessarily empirical but may sometimes be quite valuable to the organic chemist. In the vast amount of work which has been done by workers in infrared and Raman spectra certain interesting results have been obtained. Thus, for example, one finds such groups as C−H, C−C, and C=C having practically the same oscillation frequencies regardless of wide variations in the nature of neighboring atoms and atomic groups.

The extension of infrared and Raman methods to the study of highly polymerized materials such as rubber has been limited, even though these methods offer a means of gaining information concerning both the primary chemical linkages and also the forces between units without disturbing either. Spectroscopic studies have been desirable, but until recently experimental difficulties have prevented them. Early attempts to secure a Raman spectrum ended in failure as a result of continuous background radiation which prevented the observation of distinct Raman lines.[2] This continuous background was attributed by Signer and Weiler to fluorescent end groups or to fluorescent impurities in the samples used. More recently Gehman and Osterhof[3] have overcome these difficulties by studying the spectra of rubber in carbon tetrachloride and in carbon disulphide. These investigators were able to secure an excellent Raman spectrum for rubber with the possibility of the obscuration of a few weak lines by fluorescent background and by coincidence with solvent lines.

Even the improved Raman methods leave something to be desired, since results obtained with solutions are never as satisfactory as those obtained with a pure compound. Disturbing effects caused by interactions between solvent and solute are often in evidence. Hence it was decided to attempt the application of infrared methods to this problem. At first glance, it would appear that the difficulties involved in the infrared approach are even greater than in the Raman work. As in the Raman studies one is faced immediately with the problem of a continuous background of apparent absorption,

[1] R. B. Barnes, Rev. Sci. Inst. **7**, 265 (1936).

[2] R. Signer and J. Weiler, Helv. Chim. Acta **15**, 649 (1932); D. Franklin and E. R. Laird, Phys. Rev. **36**, 147 (1930); W. F. Busse, J. Phys. Chem. **36**, 2862 (1932); S. D. Gehman, J. Am. Chem. Soc. **57**, 1382 (1935).

[3] S. D. Gehman and H. J. Osterhof, J. Am. Chem. Soc. **58**, 217 (1936).

which is actually the result of scattering by surface irregularities and by colloidal particles in the rubber itself. Another difficulty arises in securing appropriate thicknesses for use in absorption measurements. The thicknesses required are in the neighborhood of a few hundredths of a millimeter, thicknesses ordinarily easily obtained with a microtome. However, a microtome cannot be used effectively on a substance having the qualities of rubber. Therefore the absorbing layers employed have to be used in the form in which they were originally deposited.

The spectroscopic methods used have been described in a previous paper.[4] A Hilger infrared spectrometer with a rocksalt prism was used as a resolving instrument and the effective slit-widths were 0.04μ at 3μ and 0.03μ at 6μ. In order to have the spectra of simpler compounds of a similar chemical nature available for comparison with the rubber spectrum, the absorption of isoprene and styrene was measured. Isoprene is the unit cell in the highly polymerized rubber complex, and styrene has a number of similar properties. Absorbing layers of these liquids 0.06 mm in thickness were enclosed in absorption cells equipped with fluorite windows. The other substances studied were natural rubber, vulcanized rubber of low sulphur content, rubber hydrochloride, and polymerized butadiene. The simple gum rubber was prepared from latex in this laboratory, while the vulcanized rubber was a commercial product. The rubber hydrochloride, the isoprene, and the styrene were obtained from the Goodyear laboratories. The butadiene polymer was supplied by Dr. H. A. Tanner and was in the early stages of polymerization. The absorbing layers had the following thicknesses: natural rubber 0.14 mm, vulcanized rubber 0.07 mm, rubber hydrochloride 0.09 mm, and the butadiene polymer 0.06 mm. The last-named compound had the appearance of a clear, extremely viscous liquid, and the absorbing layer to be studied had to be deposited upon a fluorite plate. Owing to the extreme viscosity of the sample, it was difficult to obtain a smooth layer and considerable scattering took place at the surface.

In Fig. 1 are shown curves representing the

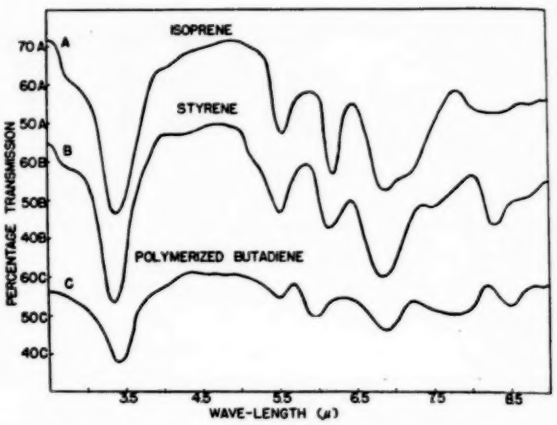


FIG. 1. The percentage transmission of isoprene, styrene, and polymerized butadiene. Region: 2.5μ to 9.0μ.

percentage transmission of isoprene, styrene, and polymerized butadiene in the region from 2.5μ to 9.0μ. It will be noted that the curves show the same general characteristics: intense absorption at 3.5μ and 7μ, double absorption maxima in the 5.5μ–6.5μ region, and weak bands near 8.5μ. The bands in the first two curves are sharp and intense, whereas in the curve for polymerized butadiene the absorption maxima are broader and less pronounced. This latter effect is due to scattering by surface irregularities.

Fig. 2 shows the percentage transmission of the various types of rubber studied. These curves are very similar to those of Fig. 1 in most ways. However, it will be readily seen that there are radical changes in the region between 5.5μ and 6.5μ as compared with the same region in the first figure. Also there are additional minor absorption maxima beyond 6.5μ. In the curve for rubber hydrochloride there is an intense band at 8.25μ which does not appear in the upper curves. Another point of interest is the broadness and lack of sharp definition of the bands in the spectrum of natural rubber especially in the 3.5μ region, an effect resulting from the scattering action of colloidal particles since the surfaces of the absorbing layers were quite smooth.

The frequencies of the observed absorption maxima are given in Table I along with a list of the probable origins of the most important frequencies and with the conventional chemical formulae of the compounds. The frequencies given in italic type are the most intense. In attributing the observed absorption to definite

[4] W. Gordy and D. Williams, J. Chem. Phys. **3**, 664 (1935).

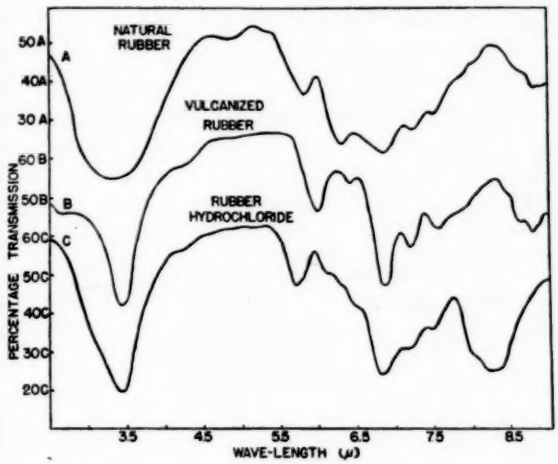


FIG. 2. The percentage transmission of natural rubber, vulcanized rubber, and rubber hydrochloride. Region: 2.5μ to 9.0μ.

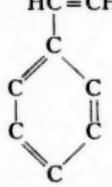
oscillation mechanisms the author has been guided by the general rules as summarized by Barnes in the article mentioned above. These empirical rules have been developed through the study of data obtained by a number of investigators. Thus one finds the following average values in a number of different compounds:

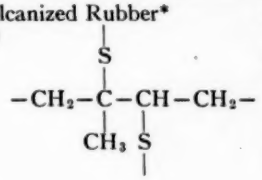
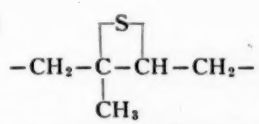
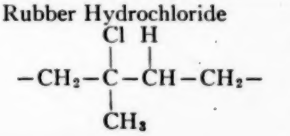
(1) $\nu(C-H) \backsimeq 3000$ cm^{-1}
(2) $\delta(CH_{2,3}) \backsimeq 1440$ cm^{-1}
(3) $\nu(C=C) \backsimeq 1500$ to 1800 cm^{-1}
(4) $\nu(C-C) \backsimeq 900$ cm^{-1}

Barnes gives the value 1440 cm^{-1} only for the deformation frequency of CH_2, but in a study of Coblentz' extensive work on organic compounds the author finds that the CH_3 group has a band in the same region.[5] Also Barnes gives the value for the linear vibration of C−C as 980 cm^{-1} while the author finds the average value to be nearer 900 cm^{-1}. On the basis of these empirical rules the interpretations have been made.

The frequencies of isoprene and natural rubber listed in the table are in agreement with the Raman values obtained by Gehman and Osterhof.[3] These investigators were able to obtain weak Raman lines corresponding to frequencies which were not detected in the present work. The

TABLE I. *Frequencies of the observed absorption maxima.*

Chemical Formula	Characteristic Frequencies	Probable Origin
A. Isoprene $CH_2=C(CH_3)-CH=CH_2$	*2985* cm^{-1}	ν(C−H)
	1800	2ν(C−C)
	1610	ν(C=C)
	1460	$\delta(CH_2, CH_3)$
	1390	
	1335	
	1155	
	1145	
B. Styrene 	*2995* cm^{-1}	ν(C−H)
	1820	2ν(C−C)
	1625	ν(C=C)
	1460	$\delta(CH_2)$
	1390	
	1335	
	1205	
	1140	
C. Polymerized Butadiene $-CH_2-CH=CH-CH_2-$	*2920* cm^{-1}	ν(C−H)
	1820	2ν(C−C)
	1680	ν(C=C)
	1460	$\delta(CH_2)$
	1390	
	1335	
	1160	
	1135	

Chemical Formula	Characteristic Frequencies	Probable Origin
D. Natural Rubber $-CH_2-C(CH_3)=CH-CH_2-$	*2980* cm^{-1}	ν(C−H)
	1725	2ν(C−C)
	1600	ν(C=C)
	1460	$\delta(CH_2, CH_3)$
	1390	
	1335	
	1160	
	1135	
E. Vulcanized Rubber* (a) 	*2900* cm^{-1}	ν(C−H)
	1665	2ν(C−C)
	1560	ν(C=C)
	1460	$\delta(CH_2, CH_3)$
	1390	
	1325	
	1160	
	1135	
(b) 		
F. Rubber Hydrochloride 	*2900* cm^{-1}	ν(C−H)
	1755	2ν(C−C)
	1460	$\delta(CH_2, CH_3)$
	1390	
	1335	
	1210	2ν(C−Cl)

* Formulae given by A. L. Henne and A. F. Shepard, J. Am. Chem. Soc. **56**, 1326 (1934).
[5] W. W. Coblentz, Carnegie Inst. of Wash. Pub. No. 35 (1905).

slight differences between the values obtained for the principal frequencies by the different methods may be due to the action of the solvent used in the Raman work. The major differences between the results, however, is the appearance in the infrared spectrum of a band corresponding to a frequency of 1800 cm^{-1}. This band has been classified as the first harmonic of a C−C vibrational frequency, but this harmonic frequency evidently does not give rise to a Raman line. It will be noted that intense bands appear in the vulcanized rubber and the rubber hydrochloride spectra at 1665 cm^{-1} and 1755 cm^{-1} respectively. Since most of the double bonds have been broken, these bands have likewise been attributed to the first harmonic of a C−C vibration, the frequency of the vibration having been decreased by the heavy sulphur and chlorine atoms present. The band appearing at 1210 cm^{-1} in the spectrum of rubber hydrochloride probably arises from a vibration in which a chlorine atom is involved, as an intense band of this frequency does not appear in the spectra of the other compounds studied. As mentioned above, the sulphur content of the sample of vulcanized rubber is low, and hence some double bonds remain unbroken. The weak band corresponding to a frequency of 1560 cm^{-1} may be due to a C=C vibration having a frequency lower than the usual value as a result of heavy neighboring units.

It has been the purpose of the writer to demonstrate the applicability of infrared technique to the problems of rubber chemistry rather than to obtain data on samples of extreme purity. The results seem to indicate that valuable information can be gained by infrared methods. The measurements made with a prism spectrometer do not show the presence of all the minor frequencies obtained in Raman work, but the necessity for a solvent with all its disturbing effects is removed. It should prove interesting to observe the effects of stretching on the absorption spectrum of rubber, since it has been shown[6] that the mechanism of elastic stretch is intimately connected with the structure of the rubber molecule itself. The effects of various degrees of vulcanization can likewise be readily determined by infrared methods.

The author wishes to acknowledge his indebtedness to Professor E. K. Plyler of the University of North Carolina for the use of his laboratory facilities and to Professor Edward Mack, Jr., and Dr. H. A. Tanner for supplying certain of the samples studied and for offering many helpful suggestions.

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[6] E. Mack, Jr., J. Am. Chem. Soc. **56**, 2757 (1934).

RHEOLOGY SECTION

Note on Heat Effects in Capillary Flow[1]

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(Received August 20, 1936)

Approximate mathematical solutions are given for the temperature distribution over the cross section of a capillary tube under two extreme conditions, (1) complete adiabatic flow, and (2) thermal equilibrium. By *complete* adiabatic flow is meant an ideal condition in which there is no heat conduction although sufficient time has elapsed since the beginning of flow to permit any particle of the fluid to travel the entire length of the tube. By thermal equilibrium is meant, in the present connection, a steady state in which the heat due to viscous resistance is conducted radially outward as fast as it is generated. In each case the mean temperature rise at efflux is calculated by integration. In the case of thermal equilibrium, formulas are also given for the decrease in apparent viscosity due to heat effects with increasing rate of flow.

INTRODUCTION

MANY years ago P. W. Bridgman observed that a fine jet of kerosene issued from a high pressure cylinder into the air in the form of smoke.[2] This combustion was presumably due to the heat generated by the leakage. It was afterward pointed out by the writer, in connection with the problem of high pressure capillary flow,[3] that the adiabatic temperature rise at efflux in a fluid of constant density is independent of the dimensions of the capillary or the viscosity of the fluid, and is given by

$$T_m = P/h. \tag{1}$$

In this equation P is the pressure drop, or the inlet pressure when discharging into the free atmosphere; and h the heat capacity (in work units) per unit volume, or the product of the specific heat into the density. For example, if we take the specific heat of kerosene equal to 0.5 and sp. gravity 0.8, we find h is approximately 17 kg·cm/cm³·°C, or more simply 17 kg/cm²·°C. On the basis of Eq. (1), therefore, the efflux temperature would rise 100°C for every 1700 kg/cm² of pressure drop.

More recently L. H. Adams has given the necessary formulas for computing the temperature rise in three different types of adiabatic flow.[4] His equation for the *isenkaumic* or porous-plug type of flow reduces to Eq. (1) above when the density is treated as constant. It is based on the usual thermodynamic reasoning without detailed analysis of the temperature distribution over the cross section.

The problem is fundamental in rheology since it is impossible to maintain viscous flow without some dissipation of energy into heat. It is of special importance in connection with the search for deviations from Newton's law at high rates of shear, in order to distinguish real deviations from apparent deviations due to heat effects.

Albert Kingsbury and others[5, 6] have investigated heat effects in lubricating films. The following study of capillary flow is analogous to the previous work on lubricating films, and especially so in the case of thermal equilibrium. The principles underlying the present calculations are generally accepted, and are indirectly supported by Kingsbury's experiments.

COMPLETE ADIABATIC FLOW

We may begin by considering the ideal condition in which there is no heat conduction

[1] Presented at the Sixth Annual Meeting of the Society of Rheology, Philadelphia, Pa., October 19–20, 1934.

[2] Personal communication from P. W. Bridgman.

[3] M. D. Hersey, J. Wash. Acad. Sci. **6**, 525 (1916).

[4] L. H. Adams, "Temperature Changes Accompanying Isentropic, Isenergic, and Isenkaumic Expansion," J. Wash. Acad. Sci. **12**, 407 (1922).

[5] A. Kingsbury, "Heat Effects in Lubricating Films," Mech. Eng. **55**, 685 (1933).

[6] M. D. Hersey, *Theory of Lubrication* (John Wiley & Sons, Inc., New York, 1936), pp. 115–119.

although sufficient time has elapsed for every particle of the outflowing liquid to have traveled the entire length of the tube. This may be termed *complete* adiabatic flow as distinguished from the more usual condition in which some of the layers close to the wall have traveled only a part of that distance. The latter may be called *incomplete* adiabatic flow.

The validity of Eq. (1) under the condition of complete adiabatic flow, without acceleration, change of elevation, or change of density is a consequence of the first law of thermodynamics. The work done by the inlet pressure P on each unit of volume entering the capillary is gradually converted into heat, which is made evident by the rise of temperature at the outlet. The amount of this work, per unit volume, is numerically equal to the inlet pressure. The corresponding rise of temperature is equal to the work per unit volume, or pressure, divided by the heat capacity per unit volume provided heat is measured in work units.

The application of Eq. (1) is not limited to simple viscous liquids, but when proceeding to the question of the internal temperature distribution it is necessary to specify the rheological equation[7] of the material. The following analysis will be restricted to liquids following Newton's law, according to which the rate of shear is directly proportional to the shearing stress.

Let H denote the time rate at which heat is being generated per unit volume at any point in the liquid, due to viscous resistance; while h as before represents the heat capacity of the liquid per unit volume. Then the temperature rise T at this point after a time t is given by

$$T=(H/h)t=(H/h)(y/v), \tag{2}$$

where y is the distance traveled in the time t at a velocity v.

Lamb in his treatise on hydrodynamics[8] gives a general theorem for the power dissipated in a viscous fluid in terms of the space derivatives of the velocity components u, v and w. As applied to capillary flow Lamb's theorem may be written, to a close approximation,

$$H=\mu(dv/dx)^2; \tag{3}$$

in which μ is the viscosity and v the velocity at any radial distance x from the axis of the tube. Thus dv/dx is the negative of the velocity gradient, or rate of shear, for if the liquid adheres to the wall of the tube, the velocity increases with diminishing values of x.

It is commonly shown in the derivation of Poiseuille's law[9] that the velocity gradient at any radius x is given by

$$-\frac{dv}{dx}=\frac{1}{2}\left(\frac{P}{L}\right)\frac{x}{\mu}, \tag{4}$$

where P is the inlet pressure and L the length of the capillary. This follows from Newton's law since the expression $(x/2)P/L$ represents the shearing stress at radius x. Integrating (4) with $v=0$ when $x=r$, in which r denotes the radius of the tube,

$$v=\frac{1}{4\mu}\left(\frac{P}{L}\right)(r^2-x^2). \tag{5}$$

Substituting from (4) into (3) and then from (3) and (5) into (2) leads at once to the required temperature distribution formula,

$$T=\frac{P}{h}\left(\frac{x^2}{r^2-x^2}\right)\frac{y}{L}, \tag{6}$$

giving the temperature rise T at any point whose cylindrical coordinates are x and y.

To determine the volumetric mean temperature rise T_m at the outlet we set $y/L=1$ in Eq. (6) and evaluate the integral

$$T_m=\frac{1}{Q}\int TdQ=\frac{1}{Q}\int TvdA, \tag{7}$$

where Q denotes the rate of efflux in volume units per unit time, and dA is an element of area. From Poiseuille's law, or by integrating Eq. (5),

$$Q=\frac{\pi}{8}\left(\frac{P}{L}\right)\frac{r^4}{\mu}. \tag{8}$$

Taking $2\pi xdx$ for dA and integrating (7) from $x=0$ to $x=r$, after substituting the appropriate expressions for v, T, and Q from (5), (6), and (8), respectively, leads directly back to Eq. (1).

[7] M. D. Hersey, J. Rheol. **3**, 196 (1932).
[8] H. Lamb, *Hydrodynamics*, sixth edition (Cambridge University Press, 1879, 1932).
[9] See, for example, reference 6, pp. 26–28.

Thermal Equilibrium

After a steady state has been established such that the heat is conducted radially outward as fast as it is generated, and assuming the tube long enough so that conditions are practically the same at every cross section, we have for the power dissipated within a radial distance x from the axis the expression

$$L\int_0^x H(2\pi x dx).$$

By Fourier's law this must be equal to

$$-k(dT/dx)2\pi xL,$$

in which k is the thermal conductivity of the liquid, and T the temperature elevation at the radius x relative to the temperature at the inside wall of the tube. From Lamb's theorem in conjunction with Eq. (4),

$$H=(x^2/4\mu)(P/L)^2. \tag{9}$$

We next equate the two expressions and integrate, after substituting for H from Eq. (9). Finally solving for T, we obtain the desired relation

$$T=\frac{G^2r^4}{64\mu k}\left(1-\frac{x^4}{r^4}\right), \tag{10}$$

in which G has been written for the pressure gradient P/L. This gives the temperature distribution over the cross section under thermal equilibrium conditions, assuming, as before, that the viscosity μ may be treated as a constant to the degree of approximation required. Putting $x=0$ we find for the maximum temperature rise

$$T_0=G^2r^4/64\mu k. \tag{11}$$

This may also be written

$$T_0=(\mu/k)\bar{v}^2, \tag{12}$$

in which $\bar{v}$ denotes the mean velocity $Q/\pi r^2$. Eq. (12) is similar in form to the equation for the temperature drop across a lubricating film, as indeed might be expected from dimensional requirements.

Integrating (10) by the procedure symbolized in Eq. (7) to obtain the mean temperature rise at efflux we find

$$T_m=\frac{5}{384}\left(\frac{G^2r^4}{\mu k}\right)=\frac{5}{6}\left(\frac{\mu}{k}\right)\bar{v}^2. \tag{13}$$

More precise results when desired may be obtained by a method of successive approximations, taking into account the change in viscosity with temperature. An alternative method of derivation is applicable both to the adiabatic and equilibrium problems, in which the work done upon a selected portion of the liquid by the hydrostatic pressures and shearing stresses is calculated step by step, without the aid of Lamb's theorem. From a physical point of view the step by step calculation is possibly more instructive and satisfactory although not so short.

The Change in Apparent Viscosity

When viscosities are computed from flow-pressure observations by the direct application of Poiseuille's law, disregarding the possibility of a nonuniform viscosity over the cross section, the result obtained is commonly known as the *apparent* viscosity. Denoting this by μ_a we have as a matter of definition,

$$\mu_a=\frac{\pi}{8}\left(\frac{P}{L}\right)\frac{r^4}{Q}. \tag{14}$$

Let μ_1 denote the viscosity at the wall temperature. If this temperature remains constant and the liquid follows Newton's law, μ_1 is a constant and the ratio μ_a/μ_1 is a convenient dimensionless magnitude for use in describing the change of apparent viscosity due to heat effects. The apparent viscosity ratio is equal to unity when the viscosity is uniform, but would be expected to fall below this value for a liquid subject to heat effects.

Let n denote the negative of the viscosity-temperature slope, i.e., $n=-d\mu/d\theta$ where θ is the temperature of the liquid. Then under thermal equilibrium conditions it can be shown that

$$\frac{\mu_a}{\mu_1}=\frac{1}{1+\frac{1}{2}(n/k)V^2}=\frac{1}{1+(r^2/32)(n/k)R_1^2}, \tag{15}$$

where V is the mean efflux velocity $Q_1/\pi r^2$ com-

puted from Poiseuille's law for a uniform viscosity equal to μ_1; and R_1 is the corresponding rate of shear at the wall, $4V/r$. From (15) the apparent viscosity ratio is equal to unity when $n=0$ or $V=0$, and approaches zero as V approaches infinity.

To derive (15) we may start with a simplified expression for the viscosity-temperature relation in terms of two constants a and b,

$$\mu=a/(\theta-b), \tag{16}$$

which will be sufficiently exact for small variations from the wall temperature θ_1. This may also be written

$$1/\mu=\theta/a-b/a, \tag{17}$$

and so for the viscosity at the wall temperature

$$1/\mu_1=\theta_1/a-b/a. \tag{18}$$

The relation connecting the variable temperature θ with the wall temperature θ_1 and the previously mentioned temperature rise T is by definition

$$\theta=\theta_1+T. \tag{19}$$

Substituting from (19) into (17) and making use of (18) to eliminate θ_1, we find

$$1/\mu=T/a+1/\mu_1. \tag{20}$$

This connects the variable viscosity μ with the wall viscosity μ_1 and the temperature rise T. Substituting now from (10) into (20) and then into (4) and integrating twice gives for the rate of efflux under thermal equilibrium conditions

$$Q=\frac{\pi}{8}\cdot\frac{r^4}{\mu_1}\cdot G\left(1+\frac{G^2r^4}{128ak}\right). \tag{21}$$

The expression in front of the parentheses will be recognized as the flow rate computed from Poiseuille's law for a uniform viscosity μ_1. This may be designated Q_1. In a similar manner Gr^2 may be identified with $8\mu_1Q_1/\pi r^2$ or $8\mu_1V$. Differentiation of (16) gives

$$d\mu/d\theta=-n=-\mu^2/a. \tag{22}$$

Hence at temperatures close to the wall temperature, such that to a first approximation $\mu=\mu_1$, we have

$$a=\mu_1^2/n. \tag{23}$$

Rewriting (21) in terms of Q_1, V, and n,

$$Q=Q_1[1+\tfrac{1}{2}(n/k)V^2]. \tag{24}$$

But from (14) in conjunction with the definition of Q_1 above we know that

$$\mu_a/\mu_1=Q_1/Q. \tag{25}$$

Solving (24) for the ratio Q_1/Q and substituting in (25) leads to Eq. (15), which was to be proved.

It is also of interest to express the apparent viscosity ratio in terms of the apparent rate of shear at the wall, defined by

$$R_a=(4/\pi r^3)Q. \tag{26}$$

Eq. (26) gives the true rate of shear at the wall when the viscosity is uniform. Let the apparent viscosity ratio μ_a/μ_1 be denoted by Y; then from (25) and (26)

$$Q_1=QY=(\pi r^3/4)R_aY. \tag{27}$$

Replacing V in (15) by its equivalent $Q_1/\pi r^2$ or $(r/4)R_aY$, and at the same time replacing μ_a/μ_1 by Y, we find (15) reduces to

$$Y=\frac{1}{1+(r^2/32)(n/k)Y^2R_a^2}; \tag{28}$$

or more simply

$$Y=1/(1+X^2Y^2), \tag{29}$$

from which

$$X=(1/Y)[(1-Y)/Y]^{\frac{1}{2}}. \tag{30}$$

In Eqs. (29) and (30) the new variable X is proportional to the apparent rate of shear at the wall and is defined by

$$X^2=(r^2/32)(n/k)R_a^2. \tag{31}$$

From (30) when $X=0$, $Y=1$; when $X=\infty$, $Y=0$; for small values of X we find that $Y=1-X^2$ while for very large values, Y is inversely proportional to the $\frac{2}{3}$ power of X. Thus the curve drops off from the initial value, $Y=1$, at first slowly, then more rapidly, passing through a point of inflection with increasing values of X and approaching zero asymptotically as the rate of shear continues to increase.

According to Eq. (30) the point of inflection comes at $X=0.537$, for which value $Y=5/6$.

Substituting in (31) and solving for the apparent rate of shear we find approximately

$$R_a = (3/r)(k/n)^{\frac{1}{2}}. \qquad (32)$$

Thus for example in the case of a light Pennsylvania oil of about 150 centipoises at 25°C, for which in round numbers $n = 0.075$ poise per degree and $k = 3.2(10)^{-4}$ cal/sec·cm·°C, or 13,400 erg/sec·cm·°C, we have in c.g.s. units $R_a = 1270/r$. With a capillary radius of 0.01 centimeter we should therefore expect the point of inflection to occur at an apparent rate of shear of 127,000 reciprocal seconds under thermal equilibrium conditions, at which time the apparent viscosity would have dropped to 5/6 of its initial value.

Conclusion

Approximate formulas have been developed for the temperature distribution and other characteristics of capillary flow due to heat effects, under certain idealized conditions which have been defined. Some of the directions in which further study would be desirable are (1) mathematical solutions for incomplete adiabatic flow; (2) solutions for the general case intermediate between the adiabatic and equilibrium conditions; (3) estimates of the time required to approximate a steady state; (4) analysis of the optimum experimental conditions for investigating deviations from Newton's law; and (5) calculation of heat effects in plastic and other non-Newtonian materials.

The Relation Between Absolute Viscosity and Penetration of Asphaltic Bitumens

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(Received July 24, 1936)

The relationship between absolute viscosity and penetration for asphaltic bitumens has been reinvestigated. With purely viscous materials in a wide range of penetration figures (5 to 250) a general relation exists. It is found, however, that the depth of penetration depends somewhat upon the conditions under which the measurements are made. Inadequate adhesion of the bitumen to the penetration needle increases the penetration. This effect, however, is not great and is the same for all purely viscous bitumens of the same penetration. Penetration depth determinations were also made with elastic bitumens. Here the final penetration depth is increased by interruptions of the determination as a consequence of the dissipation of the elastic tension during interruption. It is concluded that Traxler, Pittman, and Burns in their experiments have overlooked the elastic behavior of some of their bitumens and that therefore their criticism of the relation deduced by us between penetration and absolute viscosity is not valid.

INTRODUCTION

SOME time ago Traxler, Pittman and Burns[1,2] published a number of absolute viscosity determinations relating to asphaltic bitumens, which determinations were compared with the penetration values of these bitumens. They came to the conclusion that the formula for the relation of absolute viscosity and penetration as given by one of us (S)[3,4] *viz.*:

$$\eta = 5.13 \times 10^9 / \text{pen.}^{1.93} \qquad (1)$$

does not always hold good. In this formula η is the absolute viscosity in poises, pen. the penetration during 5 sec. and with a load of 100 g, with the apparatus standardized by the A.S.T.M.[5] The formula can be applied with penetration figures larger than 5.

As was stated when deducing the formula (reference 3, page 188), its application is only permitted for materials of a purely viscous character; as soon as the liquid is non-Newtonian, or shows elastic properties (reference 4, page 522) it is no longer valid. Further, we stated (reference 3, page 181) that the accuracy of our determinations of the absolute viscosity was usually 5–10 percent. The measurement of the penetration in general shows differences of at most 5 percent, so that no better agreement between experiment and a given formula can be expected than to within about 10–15 percent.

In reply to the above criticism some determinations and observations on the penetration test are given below, which are in part due to an interchange of ideas with Traxler and Pittman. These determinations were also made with the aid of the apparatus specified by the A.S.T.M. On the strength of these determinations we shall revert to this criticism at the end of the present article.

FACTORS AFFECTING THE PENETRATION MEASUREMENT

When, with purely viscous materials, the penetration needle adheres well to the bitumen, the flow in the bitumen is conclusively determined and there must be a direct relation between the viscosity and the penetration depth.* The factors that determine the depth the needle pierces into the material are then the load $P(mlt^{-2})$, the viscosity $\eta(ml^{-1}t^{-1})$, the duration of the test t and the dimensions of the needle etc., (l) so that in the formula P, η and t must occur as

$$Pt/\eta. \qquad (2)$$

If the penetration depth is small or the load large, however, this formula proves not to tally exactly with the measurements (reference 3, page 208), but if the former is larger, it does.

[1] Pittman and Traxler, Physics **5**, 221 (1934).
[2] Traxler, Pittman and Burns, Physics **6**, 58 (1935).
[3] Saal and Koens, J. Inst. of Petrol. Tech. **19**, 176 (1933).
[4] Proc. World Petrol. Cong., London **2**, 515 (1933).
[5] A.S.T.M. D 5/25.

* To avoid misunderstandings, we shall take "penetration" to mean the figure for 5 sec. 100 g, and "penetration depth" to mean the figures for other times and loads.

These disparities can be due to various causes: inadequate adhesion (reference 3, page 188), for instance, a film of water between the needle and the bitumen, or symptoms of brittleness, that is to say, the possibility exists that the needle breaks its way through the bitumen. In these cases it is possible that formula (2) no longer holds good.

The first point may be investigated in various ways. For instance, we carried out determinations in which the penetration tin was immersed in some liquid other than water. We took glycerol (high viscosity) and a solution with a capillary active material, *viz.* a 2 percent solution of sodium oleate in water. The measurements were made at 25°C upon the following bitumens:[6]

A. Highly susceptible to changes of temperature and not plastic ("*Z*" type).
B. Moderately susceptible to changes of temperature, plastic and elastic ("*N*" type).
C. Little susceptible to changes of temperature, strongly plastic and elastic ("*R*" type).
D. Little susceptible to changes of temperature, strongly plastic and elastic ("*R*" type).

The results are given in Table I.

The figures obtained with the soap solution are higher than those found in glycerol or water. It follows from these figures that the adhesion between bitumen and needle can easily be influenced; but it cannot be concluded that in the case of water the adhesion can be inadequate.

This can be done by another kind of test, in which during the determination of the penetration depth several interruptions are incorporated. For the purpose in question a nonelastic and nonplastic bitumen must be used in this kind of testing, as otherwise complications arise to which we shall revert further on. Two series of determinations were carried out; one of uninterrupted penetrating, for 5, 25, 60 and 100 sec., respectively; the other starting with a period of penetrating for 5 sec., followed successively by an interval of waiting for 5 minutes, 20 sec. of penetrating, another interval of 5 minutes, another 20 sec. of penetrating, and so on, alternately. The results obtained are given in Table II and plotted in Fig. 1: the *a* and *b* lines representing the determinations without interruption, the *a'* and *b'* lines those with interruptions. Each point was determined in sixfold, namely in two penetration tins, by 3 measurements in each, the maximum difference observed being 4 percent. The *a* lines show a distinctly greater penetration depth than the *a'* lines; apparently the adhesion of the bitumen to the needle, particularly at the start of the determination, is not adequate, so that especially in the *a* lines a kind of "slipping" along the needle occurs. At temperatures at which the bitumen is softer (pen. about 50), such a difference was no longer apparent, as in Fig. 1 the *b* and *b'* lines prove to coincide.

It must be remarked that it appears as though the *a* and *a'* lines approach each other after long times of penetrating. This is the consequence of the use of logarithmic plotting; actually, the

TABLE I. *Penetration determinations of bitumen in various liquids.*

Bitumen	R. & B.°C	Penetration/25°C in:		
		Water	Glycerol	Soap solution
A	52.5	21.5	21	22.5
B	70.5	17	16	18.5
C	88.0	38.5	40	46.5
D	137.0	11.5	12	13

[6] Pfeiffer and van Doormaal, "The Rheological Properties of Asphaltic Bitumens," *J. Inst. Petrol. Tech.* **22**, 414 (1936).

TABLE II. *Determination of penetration depths without and with intervals of rest.*

Bitumen		*E*	*F*	*G*
Analysis of the bitumen	Pen./25°C	16	24	3
	Melt. pt. R. & B. °C	56	52	63
	% Insol. in 60/80 gasoline	2	2	4

Temperature of the determination		25°C	34°C	25°C	34°C	45°C
Penetrating without intervals	Curve	a_1	b_1	a_2	b_2	b_3
	Pen. depth after 5 sec.	16	61	24	84	57
	25 "	31	123	46	174	120
	60 "	—	—	—	258	—
	100 "	54	251	80	—	226
Penetrating with intervals	Curve	a_1'	b_1'	a_2'	b_2'	b_3'
	Total pen. depth after 5 sec.	15.5	61	24	83	56
	25 "	26	126	40	173	117
	45 "	34	167	53	228	154
	65 "	41	199	63	267	183
	85 "	48	227	72	—	208
	105 "	53	249	80	—	229

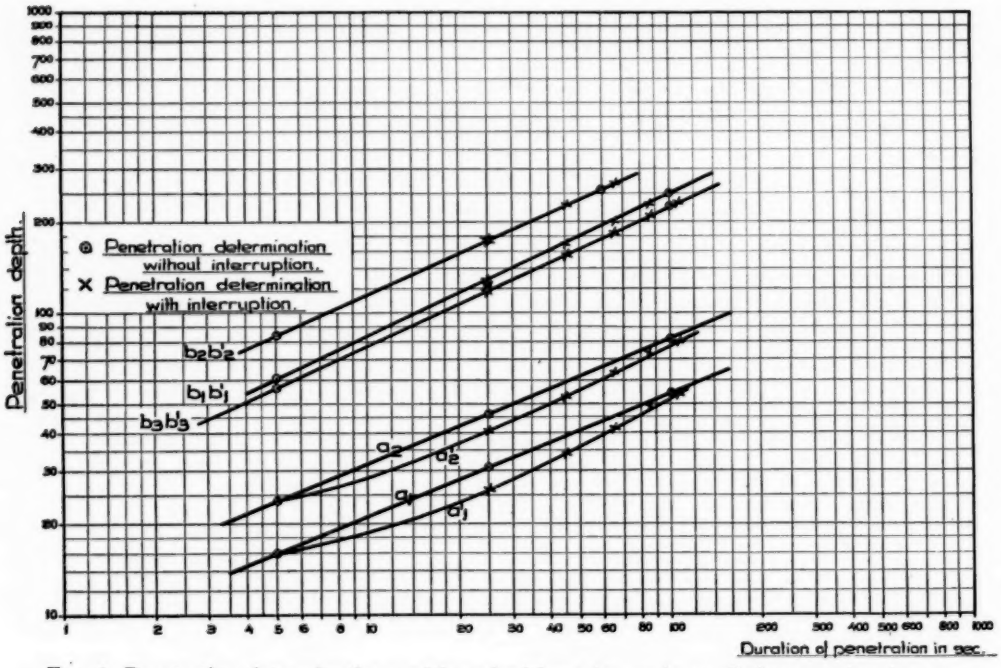

FIG. 1. Penetration determinations, with and without intervals, applied to purely viscous bitumens.

distance in horizontal direction between the a and a' lines, which belong together, remains about 5 to 10 sec.

When drawing out the needle after the determination, a corresponding phenomenon is also observed. Whereas with hard bitumens the needle when drawn from the bitumen is clean, it is found with soft bitumens that some of the part of the needle that has penetrated into the material is coated with bitumen and some of it is clean. An example: a bitumen showed a penetration of 274; after drawing the needle from the bitumen, the point up to 18.5 mm was covered with bitumen, whereas the remaining 9 mm were clean. There was a small dent round the needle, but one can hardly assume its depth to be 9 mm; 2 mm would seem more probable.

From the fact that the b and b' lines in Fig. 1 cover one another, it appears that in this range after penetrating for 5 sec. no difference in adhesion is any longer noticeable in the results of the determination; it is probable, however, that in the first seconds of this determination also a certain amount of slipping has occurred. This means that even then deviations from formula (2) are to be expected. Results published formerly (reference 3, page 208), however, showed that such deviations will be, in general, only slight. On the other hand, the validity of formula (1) is not affected at all by slipping phenomena, as this formula only gives an experimental relation between the absolute viscosity and the penetration under well-defined conditions, and this has been checked for typical examples of the few origins of crude oil that give purely viscous bitumens.

ELASTICITY

The same kind of test as described above can be used for an approximate investigation into the elastic properties of asphaltic bitumens. As already remarked, it is not possible with non-Newtonian and/or elastic liquids to show a relation between the penetration and the "viscosity," because the latter then no longer has a definite value (reference 3, page 188). Generally, in the case of deformation, the elasticity of a bitumen exhibits itself, for instance under constant shearing stress, by a higher rate of deformation at the start than it has subsequently (reference 3, page 180). In the penetration determination this means that the rate of penetrating is higher in the beginning of the 5 sec. of the test and afterwards lower if compared with a purely viscous material

of the same penetration. The slope of a penetration depth/time curve therefore, will be slighter in the case of an elastic bitumen than in the case of a nonelastic one.

Furthermore, the elastic properties will also be manifested if the determination of the penetration depth is carried out with intervals of rest. In this case it may be expected that by means of the interruptions during determination a *higher* penetration depth will be obtained (instead of a *lower* one, as was previously stated), as the elastic tensions will have an opportunity of dissipating during the intervals of rest. In Table III and Fig. 2, we give some results of such determinations.

For the sake of comparison curves b_4 and b_4', referring again to a purely viscous bitumen (H), are plotted; interruption of the measurements for some time made no difference as the bitumen was sufficiently soft. The slope of the line approximately corresponds to a quadratic relation (reference 3, page 204). Curves c and c' now illustrate the corresponding relation of a steam-refined ("*N*" type) straight-run Mene Grande bitumen (I, pen./25 = 90, R. & B. = 45.5°C). Intervals of rest during the determination prove to affect the measurement, giving a *higher* penetration with periods of rest. Moreover, the slope of these lines is slighter than of bitumen H.

Finally, curves d and d_1' indicate the same relation for a bitumen little susceptible to changes of temperature, *viz.* for a blown Venezuelan bitumen (pen./25 = 68, R. & B. = 63°C "*R*" type). The effect of an interruption is much stronger than in the case of straight-run Mene Grande. All this is shown still more clearly in curve d_2', for here the determination was repeatedly interrupted for four minutes, i.e., 5 times after penetration periods of 1 sec., 5 times after 2 sec., 5 times after 3 sec., 5 times after 4 sec., 5 times after 5 sec. and 4 times after 10 sec., so that the determination was carried out in 29 stages altogether. The slope of the d lines is again slighter than for bitumens H and I.

Products I and J were, as appeared from measurements in a Couette viscometer (reference 5, page 185), both plastic and elastic. It is, of course, not possible to indicate immediately what part of the difference between the slopes of the curves of Fig. 2 must be attributed to plasticity and what part to elasticity. The possibility of inadequate adhesion was not likely to be great, here, as after the determination the needle proved to be covered with bitumen, when it was withdrawn.

The differences in line c and d, from lines c', d_1' and d_2', respectively, are, as was already expected, to the opposite side as compared with Fig. 1. As stated before, this must be due to the fact that the elastic properties of the bitumens played a part. During the intervals of rest the tensions are dissipated; when the load is again brought to bear on the needle, the rate of penetrating is higher than without a period of rest, owing to which, therefore, during the same total time of penetration, the needle pierces deeper into the material. In this manner one can therefore easily demonstrate the elasticity by means of the penetration depth determinations. A comparison of this type of measurement with resilience curves in the Couette apparatus indeed amply proved that this may be permitted.

TABLE III. *The effect of intervals of rest upon the penetration depth of elastic bitumens.*

Bitumen		H	I	J	
Analysis of the bitumen	Pen./25°C	136	90	64	
	Melt. pt. R. & B. °C	39	45.5	63	
	% Insol. in 60/80 gasoline	1	about 15	about 25	
Temperature of the determination		20°C	25°C	25°C	
Penetrating without intervals	Curve	b_4	c	d	
	Penetration depth after				
	5 sec.	64	90	64	
	15 "	108	147	82	
	35 "	165	211	101	
	65 "	—	279	120	
	85 "	259	—	130	
	200 "	—	—	165	
	500 "	—	—	216	
	750 "	—	—	243	
Penetrating with intervals of rest	Curve	b_4'	c'	d_1'	d_2'
	Intervals of rest	2 min.	4 min.	4 min.	4 min.
	Total penetration depth after				
	5 sec.	64	90	64	71
	15 "	108	146	84	98
	25 "	140	187	98	114
	35 "	165	220	110	128
	45 "	188	249	119	139
	55 "	208	273	128	149
	65 "	226	294	136	158
	75 "	243	—	144	166
	85 "	259	—	150	171
	95 "	273	—	157	176
	105 "	—	—	162	181
	115 "	—	—	168	185

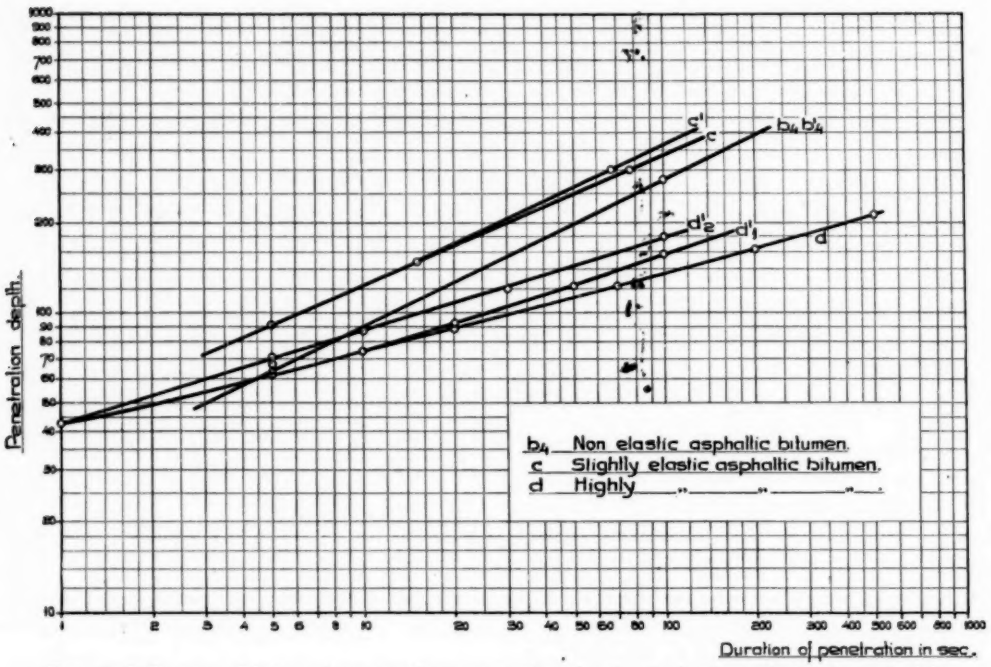

FIG. 2. Influence of intervals upon the penetration depth of plastic and elastic asphaltic bitumens.

MEASUREMENTS BY TRAXLER, PITTMAN AND BURNS

As mentioned in the beginning of this article Traxler, Pittman and Burns carried out determinations of the absolute viscosity of bitumen, namely of Panuco and Mene Grande bitumens and of Trinidad and Bermudez Native Lake asphalt, which determinations they used to check our formula (1). On the strength of the comparisons thus made they concluded that formula (1) could only be applied to obtain approximate results. The following three arguments show that this criticism is not well founded.

1. As was demonstrated above, Mene Grande bitumen shows marked elastic properties. The same thing can, as a matter of fact, be shown by resilience determinations in a Couette apparatus; in reference 4, Fig. 11, line *B* refers to a Mene Grande bitumen. In this same figure line *G* refers to a Panuco bitumen, which shows important elastic properties too. Therefore, one may not apply formula (1) for a comparison of penetration and viscosity of these bitumens as nevertheless Traxler, Pittman and Burns do. Regarding their two other bitumens we have not sufficiently accurate data at our disposal, but we are of the opinion that our Panuco and Mene Grande examples adequately show that Traxler, Pittman and Burns seem to have overlooked the effects of non-Newtonian and/or elastic behavior. So it can easily be explained how it is that they do not find one single curve for the relation between "viscosity" and penetration for these different bitumens.

2. According to Traxler, Pittman and Burns there is already an insufficient correlation between formula (1) and our own experiments (reference 3, pages 186, 187). These disparities are in our opinion, however, slight, as may be seen from Table IV, considering the accuracy of the determinations and the large range of viscosities covered.

The argument of Traxler, Pittman and Burns against this formula, that is based upon determinations of only two bitumens, does not obtain, as, according to the measurements of the writers, these two bitumens are representative of the few origins of crude oil which give purely viscous bitumens.

3. Traxler, Pittman and Burns mention (reference 2, page 60) that their bitumens are to some degree thixotropic. This means that in their viscosity determinations they may have destroyed the structure that presumably was the cause of the thixotropy, but they cannot have done so in an equal degree with the penetration determination, so that *a priori* no direct relation between these two magnitudes may be expected.

TABLE IV. *Comparison of the calculated and determined viscosities of purely viscous bitumens.*

Penetration	Viscosity in poises		Ratio $\frac{\text{Calculated}}{\text{Determined}}$
	Calculated	Determined	
4.5	2.81×10^{8}	2.75×10^{8}	1.02
12	4.24×10^{7}	4.20×10^{7}	1.01
28.5	8.9×10^{6}	9.1×10^{6}	0.88
33	6.0×10^{6}	6.8×10^{6}	0.89
63	1.73×10^{6}	1.68×10^{6}	1.03
71	1.37×10^{6}	1.26×10^{6}	1.09
150	3.23×10^{5}	3.47×10^{5}	0.93
170	2.54×10^{5}	2.4×10^{5}	1.06

The Rheology of Raw Rubber

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(Received July 11, 1936)

A viscometer of the rotating cylinder type is described which is applicable to rheological measurements of raw rubber. To make the instrument operative with such material the surfaces of the cylinders are fluted, to form rough, gripping surfaces; and pressure devices are added which compress and confine the rubber between the cylinders. At low or moderate stresses the rate of shear in hot, raw rubber follows the equation $\dot{\alpha}=A\sigma^2$. At higher stresses the rate of shear increases more rapidly with increasing stress. The elastic recovery of hot, raw rubber requires over 5 hours for completion. During most of this time the recovery angle follows the law $\alpha=A+B\log t$. The modulus of rigidity in small deformations of hot, raw rubber is only slightly less than that of soft, cured rubbers at room temperature. The viscosity of a sample of hot, raw rubber in vibration is many times less than the viscosity of the same sample in continuous shear.

INTRODUCTION

THE scientific measurement of the rheological properties of raw, or unvulcanized, rubber is a problem that has required some new methods in rheological laboratory technique. Hot, moderately milled or masticated raw rubber exhibits to a very marked degree each of the three properties of elasticity, plasticity and thixotropy. It is highly elastic (not perfectly elastic) in that if deformed and released quickly it can take a large deformation and still return to its initial form. It is highly plastic in that under proper conditions it can be deformed to any given extent permanently and without rupture. It is highly thixotropic in that its viscosity, or stiffness, is very considerably decreased by a brief mechanical working, or mastication, and the lost viscosity is largely regained again when the mastication ceases. Obviously, such a wide and varied range in rheological properties cannot be measured in either of the two types of rheological instruments, the compression and the extrusion plastometers, commonly used for raw rubber. There is no way in either instrument to determine or correct for thixotropy; and the viscosity can only be calculated with considerable uncertainty and difficulty. For example, thixotropy has not been considered in either of the already very complicated analyses of parallel plate plastometry by R. L. Peek, Jr.[1] and by J. R. Scott.[2] Peek and Erickson[3] have attempted to analyze the effects of thixotropy and elasticity in capillary tube viscometry without obtaining a complete or generally useful solution. However useful the compression and extrusion plastometers may be in factory control work, they are inadequate as scientific research instruments.

The rotating cylinder viscometer seems to be the only type of instrument that meets the requirements of the problem considered. It allows an unlimited deformation of the test material, the previous deformation history can be controlled at will, and the subsequent elastic recovery can be measured if desired. There are two serious deficiencies of the conventional cylindrical viscometer, as applied to raw rubber, in that, firstly, the rubber, being semi-solid, would be likely to slip on the moving surfaces, and secondly, if the rubber did not slip but sheared as it should, it would soon roll and climb out of the viscometer against the force of gravity. These deficiencies can be corrected, firstly, by fluting or otherwise roughening the cylindrical surfaces so that they grip the rubber and prevent slipping, and secondly, by adding means for compressing and holding the rubber in place.

The combined use of these two devices in a factory control instrument, the rotating disk plastometer, has already been described; and a rotating cylinder viscometer with similar features was referred to in the same article.[4] The cylindrical viscometer there referred to was used in the experimental researches described below. Since this instrument is so different in several respects from the conventional cylindrical viscometers and, furthermore, is designed to facilitate the measurement of thixotropy and elastic

[1] R. L. Peek, Jr., J. Rheology **3**, 345 (1932).
[2] J. R. Scott, Inst. Rubber Indus. Trans. **10**, 481 (1935).
[3] Peek and Erickson, J. Rheology **2**, 351 (1931).
[4] M. Mooney, Ind. Eng. Chem., Anal. Ed. **6**, 147 (1934). Also U. S. Pat. 2,037,529, March 14, 1936.

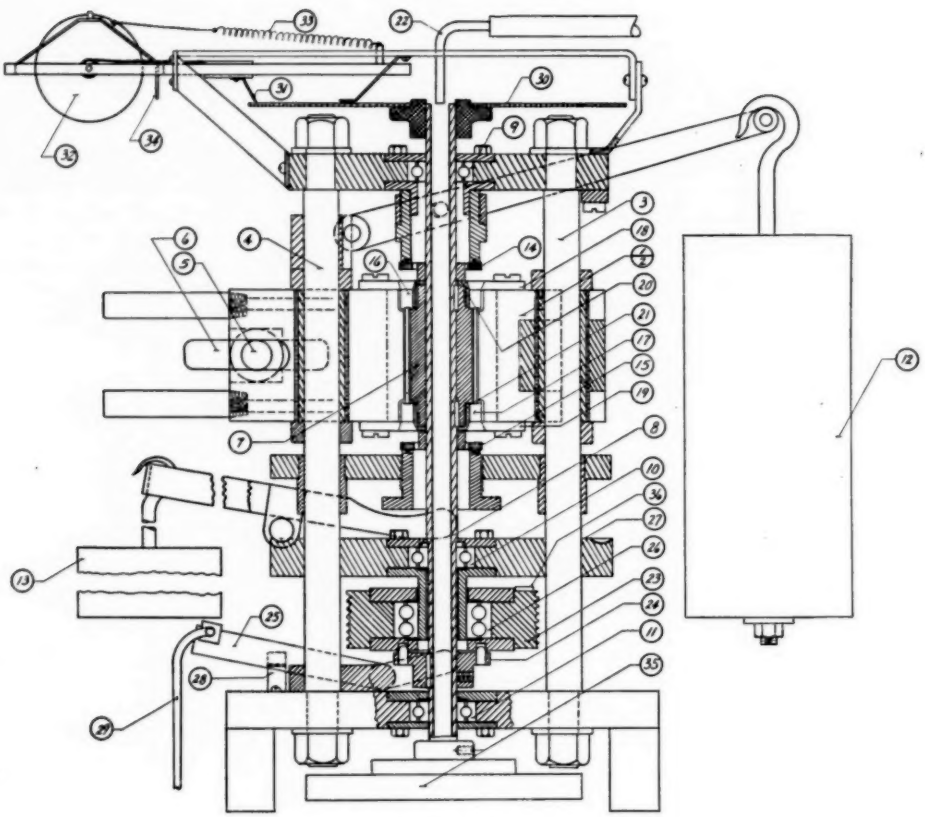

FIG. 1. The rubber rheometer.

recovery as well as viscosity, it seems appropriate to give it a new name and call it a *rubber rheometer*.

DESCRIPTION OF THE RHEOMETER

The details of the instrument are shown in Figs. 1 and 2. The outer, stationary cylinder, or stator, is split into two halves, 1 and 2, hinged on the support rod 3. When the two halves are open, rubber samples can be inserted or removed. In the closed position the two halves are locked to the support rod 4 by the bolt 5 and lock nut 6.

The inner cylinder, or rotor, 7, is mounted on the hollow shaft 8, which turns in the ball-bearings 9, 10 and 11. The surfaces of stator and rotor are each fluted longitudinally with a series of 60° V-grooves, about 90 to the inch, cut full depth, to form a series of sharp ridges.

The necessary confining pressure on the rubber sample between rotor and stator is produced by the weights 12 and 13, operating on the pressure rings 14 and 15, respectively. These rings, faced with soft vulcanized rubber pads, fit into the circular channels 16 and 17, respectively, cut into the rotor and stator above and below the fluted gripping surfaces. These channels serve as rubber reservoirs, from which reserve rubber is forced into the narrow space between the fluted surfaces as trapped air in that region works out or as rubber leaks out between the two halves of the stator. Four semi-circular, beveled guide plates, such as 18 and 19, serve to keep the rubber pressure pads from cutting or tearing on the edges of the reservoir channels. After a new sample of rubber has been inserted, the beveled plates are removed, the excess rubber above and below the stator blocks is cut away, and the beveled plates replaced again before the pressure pads are forced into the reservoir channels.

The inner surfaces of these channels are formed by the collars 20 and 21, which rotate freely on the rotor shaft.

The rotor is heated by oil which is pumped from a controlled-temperature oil bath, through

the tube 22, and which circulates through the hollow shaft by gravity. The stator is heated by oil from the same bath pumped through cavities in the stator blocks not shown in the drawings.

The driving torque operating on the rotor is obtained by driving weights connected by a small steel cable to the sheave 23. The sheave can be connected to or disconnected from the rotor shaft by means of the clutch 24, operated by the clutch handle 25. When the clutch is released, the sheave is entirely disconnected from the shaft 8, since its ball-bearing support, 26, is mounted not on the shaft, but on the plate 27. The clutch handle operates by raising the sheave to clear the pins in the clutch when the handle is down. The spring catch, 28, shown only in outline, serves to hold the handle up; but the handle can be forced down in spite of this spring, thus releasing the clutch, when a weight is dropped in a stirrup, 29, supported on the clutch handle and extending below the base of the rheometer.

The aluminum disk, 30, mounted on the upper end of the rotor shaft, carries a Central Scientific Company sensitive waxed chart, graduated in degrees. Slow or moderate rates of rotation are measured visually, with the aid of a stopwatch. At high rates of rotation, a spark record is produced on the sensitive chart by means of a Cenco Spark timer, set at a frequency of 5 sparks per second.

The stylus, 31, can be pulled radially across the face of the chart by a thread attached to a small drum mounted with a friction fit on the shaft of the fly-wheel, 32. This fly-wheel can be suddenly set into rotation by the spring, 33, when the trigger, 34, is pulled. The trigger is pulled by a string attached to the same weight that releases the clutch. It is thus possible to start the stylus moving radially across the chart just before the clutch is released and thus obtain an autographic record of elastic recovery of the sample immediately after the shearing stress is released.

The stylus serves also as the sparking point in making spark records of high rotational velocities. In this case the stylus is given a slow radial motion by means of a suitably connected, weighted string wound once around the rotor shaft. The fly-wheel, 35, is added to the lower end of the rotor shaft to increase the moment of inertia of the rotor system.

Other accessories, not shown in the drawings, include electrical devices for dropping the clutch-releasing weight, either while the rotor is still moving or at a fixed time after the rotor has been stopped. The stopping device consists merely of a sheet of red fiber, with an electrical contact, inserted between the support rod and the small stopping nut, 36, on top of the sheave. Very slow rates of rotation of the rotor are sometimes measured with a micrometer gauge with its foot resting against a small clamp temporarily attached to the edge of the aluminum disk. Mounted on the edge of the table supporting the rheometer there is a windlass for lifting the driving weights. The clutch handle has attached to it a spring which starts a stopwatch when the clutch is released.

Constants of the apparatus

Length of rotor and stator		5.08 cm (2 in.)
Radius of rotor (to top of ridges)		1.70 cm
Radius of stator " " " "		1.90 cm
Effective radius of sheave		5.05 cm
Moment of inertia of rotor system		6.03×10^4 gcm²
Mean shearing stress,	$\sigma=2.11\times10^4W$ dynes/cm²	
	W = driving weight in lb.	
Mean rate of shear,	$\frac{d\alpha}{dt}=0.162\omega$ radians/sec.	
Speed of tracer	ω = rotor velocity in degrees/sec.	
	= 20 cm/sec.	
Pressure on the rubber	$=4.4\times P$ (lb./in.²)	
	$=0.275\times P$ (kg/cm²)	

where P = the pressure weight in lb.

The above expressions for σ and $d\alpha/dt$ are calculated by means of formulas previously

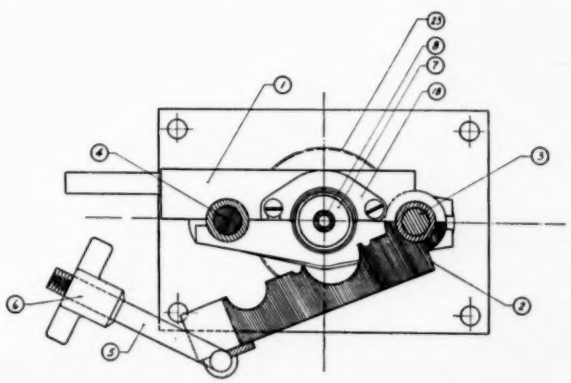

FIG. 2. The rubber rheometer.

published by the author.[5] To allow for end effects the clearance between rotor and stator was added to their actual length to obtain what was assumed to be their effective length.

Discussion of the apparatus

There are certain features of the rubber rheometer in its present form which could be improved upon. The rubber works in behind the collars 20 and 21; and these collars have to be moved up or down occasionally and cleaned out. They would give less trouble if they were designed with more free space inside between the collar and the shaft and with holes above, or below, so that the rubber that works in under the force of the pressure rings could also work out at the other end of the collar. The rubber facing on the pressure rings has to be renewed occasionally; and it could probably be satisfactorily replaced with metal faces fitting closely in the rubber reservoirs. The collars on the rotor, which were added after a solid rotor was found unsatisfactory, would probably prevent binding of the rotor by the metal pressure rings just as well as they prevent such effects with the rubber-faced pressure rings. The weights actuating the pressure rings should be augmented by screws to hold the rings firmly against the rubber; for it was found that sometimes with a large driving weight working on rather tough rubber, the rubber pushes against the pressure rings enough to force the pressure weights up a few thousandths of a cm. The resulting rate of rotation is certainly then too high; and a number of revolutions of the rotor with a lower weight are required before the rubber is compacted again and gives its former readings with the lower weight.

Experimental Results: Rheological Curves

The normal driving weight used in measuring the viscosity of raw rubber is from 9 to 45 kg (20 to 100 lb.). Weights as high as 70 kg (150 lb.) have been used and as low as 14 g (0.3 lb.). The usual pressure weight used is 9 kg (20 lb.), but with the lower driving weights it is customary to reduce or eliminate entirely the pressure weights, since there is a small but observable friction due to the pressure rings. There is friction also in the sheave, steel cable and pulley, necessarily designed for heavy loads; and for driving weights of 2 kg (5 lb.) or less the clutch is released and the driving torque is applied by a cord wrapped around the fly-wheel and passing over a light pulley with conical bearings.

When the driving torque is applied to the rotor, the speed of rotation increases at first and then attains a practically constant value in one-eighth to one-quarter of a revolution under customary operating conditions. Under low torque, constant speed is attained within a smaller rotational angle, but more time is required. Under very high torques, less time is required, but more rotation; and in extreme cases constant speed may not be attained before the driving weight hits the floor, which occurs after two complete revolutions of the rotor. No detailed study of these thixotropic effects has yet been made, and the data reported in the present paper were all obtained after essentially constant angular velocity had been attained.

Fig. 3 shows, on a logarithmic graph, the rheological curve at 100°C for a sample of pale crepe given a moderate breakdown of 10 min. on a laboratory mill. The different values of P, indicated by the various insignia as shown on the graph, are the pressure weights operating on the pressure rings. The straight part of the curve is represented by the equation

$$(d\alpha/dt)=0.9\times10^{-12}\sigma^2,$$

where $d\alpha/dt$ is the rate of shear in radians per sec., or cm per sec. per cm, and σ is the shearing stress in dynes per cm^2. If we define the fluidity φ, and the coefficient of viscosity, η, as

$$1/\varphi=\eta=\sigma/(d\alpha/dt),$$

then $1/\varphi=\eta=1.1\times10^{12}/\sigma=1.05\times10^{-6}/\alpha^{\frac{1}{2}}$.

The upward turn of the curve at the higher shearing stresses is found with all types of rubber so far examined. This feature is in general more marked the lower the temperature of the measurement and the less the break-down of the rubber.

Differences of this nature are seen in Fig. 4, which shows the rheological curves at 80° and

[5] M. Mooney, J. Rheology **2**, 210 (1931).

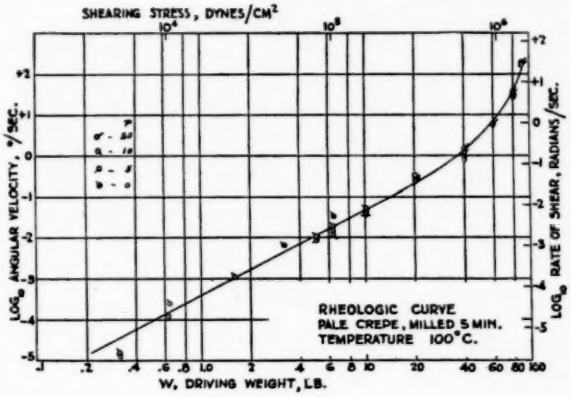

FIG. 3. Typical rheologic curve of rubber.

140°C of pale crepe with a slight, 5 min., and a severe, 30 min., break-down. At 40 kg (90 lb.) driving weight the curve for the more masticated rubber lies above the other, showing that at this stress the "harder" rubber has the lower viscosity. The arrows, indicating the sequence of measurements, show a hysteresis between 25 and 40 kg (60 and 90 lb.) load in the less milled sample. The remarkable feature about this hysteresis is that it indicates a negative thixotropy, or a hardening of the material due to mechanical working. The cause of this phenomenon is at present very uncertain. A possible explanation is that the structure of the rubber, which is inhomogeneous itself and contains foreign particles of protein and other materials, is changed at high rates of shear and a phenomenon similar to work-hardening of metals is produced.

In Fig. 5 are shown the iso-torque curves for rate of shear plotted against temperature for a sample of moderately milled pale crepe. The curves show a point of inflection and in some cases a maximum in the region of 80° to 90°C. This effect is rather surprising, but has been found in other cases, though only with slightly or moderately milled rubber. Thoroughly milled rubber does not show it.

We can explain this phenomenon to ourselves if we consider that the viscosity of rubber depends upon two properties, first, the forces of adhesion between the stable structural units, which determine how readily they yield and part or slip past each other under the shearing stress; and second, the speed with which the forces of adhesion are reestablished in the new or continuously changing arrangement of the structural units. It is well known to all rubber workers that two pieces of warm, raw rubber, when forced into contact, do not stick together nearly as firmly at first as after being left in contact for a few minutes or hours. It is not unreasonable to suppose that, likewise, in a sample of rubber subjected to shear the adhesive forces require finite time to attain their full strength between the relatively moving structural units in the material. If this is the case, then in order to explain Fig. 5 we need only to assume the proper relationships between temperature and the two properties of *ultimate* adhesive force, and the *rate* at which the ultimate adhesive force is reestablished. Thus, we may assume that the ultimate force continuously decreases with temperature and that the rate of reestablishment continuously increases with temperature; but that at about 80° to 90°C, the rate of reestablishment increases relatively faster than the ultimate force decreases. The net result is then, according to this hypothesis, that the *average* adhesive force actually maintained between the moving structural units of the rubber may increase with temperature in the indicated region, or at least not decrease as rapidly as on either side of this region. What actually happens would be expected to depend upon the rate of shear and perhaps also the shearing stress, as is shown by the experimental data.

The question has been raised whether the effects shown in Fig. 5 might result from a temperature increase in the rubber due to the viscous dissipation of energy during shearing. The question can be answered definitely in the negative. The temperature increase at the center of the sample during continuous shearing can be calculated from the thermal conductivity of rubber, the surfaces being assumed at the temperature of the rheometer. The result is

$$\Delta T\ (°\mathrm{C}) = 5.8 \times 10^{-4} W\omega,$$

W being the driving weight in pounds and ω being the angular velocity of the rotor in degrees per sec. According to this formula the temperature rise would be less than 2°C in the worst case, and is quite inadequate to account for the anomalies observed.

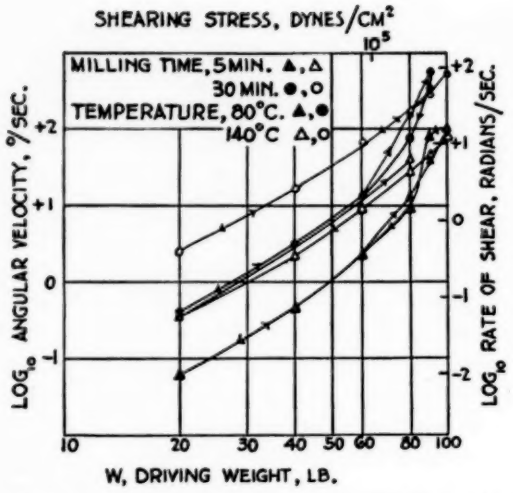

FIG. 4. Rheologic curves for pale crepe rubber, showing effect of break-down and of temperature.

ELASTIC RECOVERY

Elastic recovery in the rubber rheometer is measured by observing the reverse rotation of the rotor after the driving torque is removed. As was indicated in the description of the instrument, reverse rotation can be allowed either immediately on removal of the driving torque or after the rotor has been held stationary for a given time interval. This time interval between stoppage and permitting reverse rotation is called the *annealing time* and is denoted by t_a.

Some typical autographic records of elastic recovery are shown in Fig. 6, and the conditions preceding the recovery records are indicated in the table below the figure.

The recovery begins with the wavy portion of the curve. The waves result from the oscillations of the rotor, quickly damped, due to the elastic stress in the rubber at the moment of release.

The autographic record covers the first 0.2 sec. of recovery. After that the record is obtained by manual operation of the stylus, which produces the series of short radial lines near the periphery of the chart. (The series of points in the small circles are spark records, used for measuring the speed of rotation at high speeds.) The first manual record is made at 5 sec. after recovery begins. During this first 5 sec. the pressure rings are removed so as to eliminate friction as far as possible during recovery.

A complete elastic recovery curve is shown in Fig. 7. The time scale is linear up to 5 sec., and logarithmic thereafter. In the right-hand recovery scale the unit of one radian is equivalent to one cm shear per cm thickness. The driving weight prior to recovery was 36 kg (80 lb.), and the angular velocity of the rotor was 3.6° per sec. The recovery recorded for zero time is obtained by extrapolating the median line of the trace back to zero time. Complete recovery in this case requires over 5 hours, which is not unusual for gum rubber. This time may appear long to those who work with rubber in the factory; but it must be remembered that in the factory rubber is usually allowed to cool after calendering or extruding, and it is subjected to mechanical restraint due to its own weight. Both of these factors tend to stop elastic recovery before all the internal stresses in the rubber are released.

In Fig. 8 are shown the elastic recovery curves for pale crepe, milled 30 min., obtained at 80°C and 135°C with annealing times of 0, 0.2, 2 and 20 sec. It is seen that the recovery during the first 5 sec. is considerably reduced by annealing; but the additional recovery after 5 sec. is practically unaffected. The total recovery is less at the higher temperature and is attained more quickly.

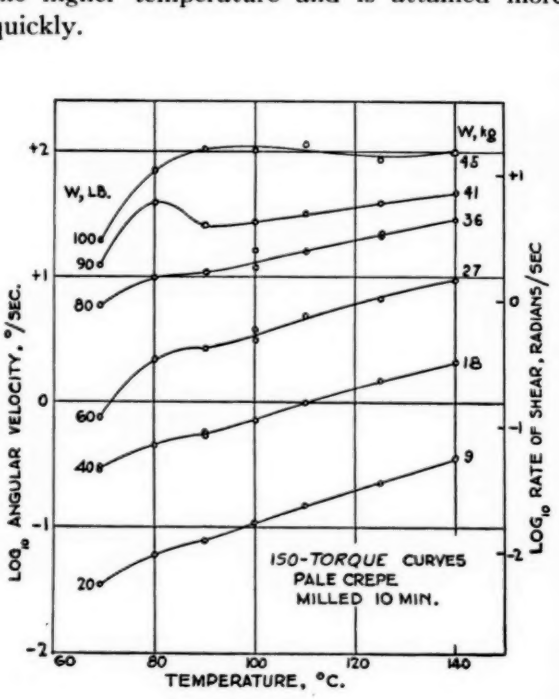

FIG. 5. Iso-torque curves, showing anomalous temperature effects.

Physical Constants in Oscillations

It is obvious that a modulus of rigidity and a coefficient of viscosity can be calculated from the frequency and damping factor of the wave form traced in the recovery curves. If we assume simple viscous damping, the free oscillations of the rotor are represented by

$$I(d^2\theta/dt^2)+f(d\theta/dt)+\beta\theta=0, \qquad (1)$$

in which θ = angular displacement of rotor in radians, t = time, I = moment of inertia, f = viscous friction constant due to the rubber, β = torque constant due to the rubber.

The solution is

$$\begin{cases}\theta=Ae^{-ft/2I}\cos 2\pi\nu t,\\ \nu=(1/2\pi)(\beta/I-f^2/4I^2)^{\frac{1}{2}}.\end{cases} \qquad (2)$$

Therefore, it can readily be shown that

$$\begin{cases}f=4\pi\nu Ik,\\ \beta=4\pi^2\nu^2I(1+k^2),\end{cases} \qquad (3)$$

where $k=(1/2\pi n)\log(\theta_0/\theta_n)$,

θ_0 and θ_n being the initial amplitude and the amplitude after n complete oscillations, respectively.

The relationships between f and β and the physical constants of the rubber are obtained by applying the formulas in the previous reference,[5] bearing in mind that the relationship between modulus of rigidity, angle of displacement, and torque corresponds exactly to the relationship between coefficient of viscosity, angular speed of rotation, and torque. The following relationships are easily deduced:

$$\begin{cases}f=4\pi l\eta_0R_1^2R_2^2/(R_2^2-R_1^2),\\ \beta=4\pi l\mu R_1^2R_2^2/(R_2^2-R_1^2),\end{cases} \qquad (4)$$

in which l = effective length of rotor or stator, R_1 = radius of rotor, R_2 = radius of stator, η_0 = coefficient of viscosity in oscillation, μ = modulus of rigidity.

From Eqs. (3) and (4), the dimensions of the rheometer and the speed of the stylus it is found that

$$\begin{cases}\eta_0=7.7\times10^2\nu k, \text{ poises},\\ \mu=1.00\times10^6(1+k^2/\lambda)\text{ dynes/cm}^2,\end{cases} \qquad (5)$$

λ being the wave-length in the recovery tracing.

[5] Reference 3, p. 210.

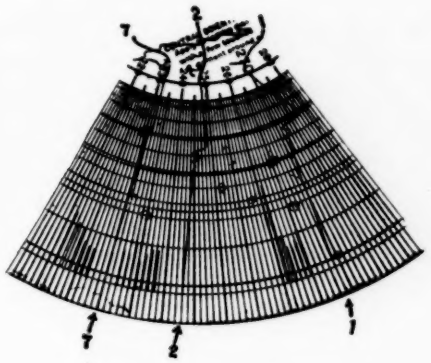

Fig. 6. Elastic recovery records.

From Eqs. (5) the following values were calculated for a sample of well-masticated smoked sheet at 97°C:

Previous Driving wt., lb.	η_0	μ
50	1.10×10^3	2.66×10^6
90	1.46×10^3	2.66×10^6

The viscosity of this same sample measured under continuous rotation is very much higher:

Driving weight		η
kg	lb.	
4.5	10	2.9×10^7
36.3	80	2.3×10^5

The modulus of rigidity is somewhat less but of the same order of magnitude as that of soft vulcanized rubbers at room temperature.

Attempts were made to determine the elastic stress in the rubber at the moment of release by measuring the curvature at the knee of the autographic recovery curve. The measurements obtained were too erratic to be of any value. The difficulty lay in the disturbing vibrations set up in the apparatus by the clutch releasing mechanism. Possibly a clutch and quick release mechanism could be designed to eliminate this

Trace No.	W, driving wt.		t_a, annealing time, sec.
	kg	lb.	
1	36	80	0
2	22	50	0
7	22	50	2

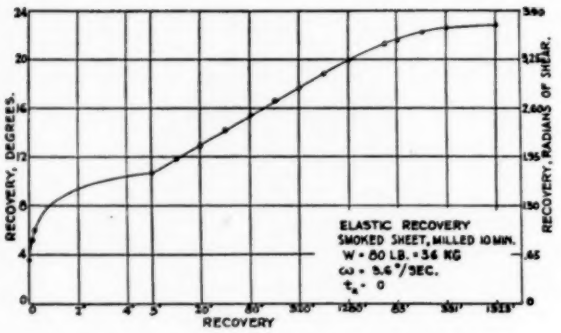

FIG. 7. Typical elastic recovery curve.

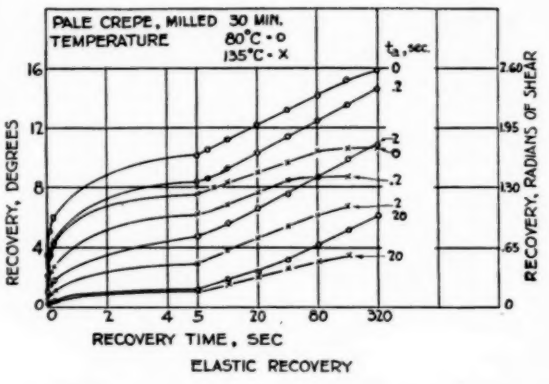

FIG. 8. Elastic recovery curves, showing effects of annealing and of temperature.

trouble, but the problem does not appear easy. The fly-wheel at the bottom of the rotor shaft was added with the purpose of increasing the period of oscillation and extending the knee beyond the duration of the disturbing vibrations; but a much larger fly-wheel would be required to accomplish the purpose.

The experimental data that have been reported here are not very precise, but at least they show that an instrument has been devised which successfully measures the fundamental rheological properties of raw rubber. Greater precision doubtless can be obtained; but high precision would probably be wasted on rubber, which varies so much with time and with previous treatment. The essential features of viscosity and elastic recovery have been developed. The relationships revealed are quite complicated, and no theories so far developed will explain the complete rheological curve and its variation with temperature, or the peculiar form of the elastic recovery curve.

A Preliminary Study of the After-Effect or Drift in Rubber Under Constant Load

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(Received June 24, 1936)

Similar vulcanized rubber bands were subjected to four different tensions which produced immediate strains of approximately two to five times their original length. During the life of the bands this elongation was augmented an additional one to two hundred percent by the so-called after-strain or drift. Observations were taken at constant temperature. The average life of the bands was about 33 weeks. No correlation was found between the magnitude of the load and the time that the specimen could bear its load. Drift for all stresses continued to the breaking point. In all cases the initial time rate of drift was comparatively high. It declined with time to a positive minimum, passed through an inflection, and then steadily increased for the remaining life of the band. The inflection occurred after some weeks or months of drift. No correlation was found between the magnitude of the load and the time of inflection in the drift rate. During the interval between one and eighty minutes, the magnitude of the drift in at least one specimen was directly proportional to the log of the time. It then deviated from the log law and for three weeks closely followed a decreasing power law.

INTRODUCTION

WHEN a suitable weight is supported by suspension from a piece of rubber, as a stationer's band, the rubber may be stretched any amount up to several times its original length, but its new length is not constant; it increases with time. The increase in length with time is variously known as "after-effect," "creep," "drift," "flow," or "time-yield." This phenomenon, which seems to have been very incompletely investigated, was probably first recognized by Dietzel[1] in 1857. Kohlrausch[2] in 1875 made an intensive study of both torsional and linear after effect in metal, glass and rubber. The loads used by Kohlrausch on rubber however, were exceedingly small and the duration of the drift was limited to one day. He came to the conclusion that drift in rubber followed a power law for the first sixty minutes. During the next decade Pulfrich[3] slightly extended the work of Kohlrausch by experimentation on a red rubber tube using elongations up to 150 percent with maximum observation time of 15 days. He concluded that the power law of Kohlrausch held for at least thirty minutes of drift. In 1903, Bouasse and Carrière[4] observed the after-effect (in pure gum and sulphur cords of 4 mm diameter and of specific gravity 0.984) under a great variety of experiments and concluded that the drift was to be expressed by an exponential or logarithmic law rather than by a power function. Both Phillips[5] and Schwartz[6] arrived at similar conclusions. More recently Ariano[7] reported that the drift proceeded at a decreasing rate which finally assumed a constant value either finite or zero. Van Geel and Eymers[8] found that for milled rubber the drift continued until the specimens broke, but that for rubber obtained from the evaporation of latex all after-effect ceased within three minutes. Shacklock[9] noted that creep took place for some hours and then reached a limit. Evidently more light needs to be cast on the problem of the drift effect in rubber. Two preliminary experiments on drift are herein considered; Part I on general trends, and Part II on more specific analysis of the effect as observed in one specimen.

PART I. EXPERIMENTAL

Twelve selected rubber bands were hung from metal hooks screwed into the ceiling of an apparatus cabinet, the shelves of which had been removed. Specially prepared indicator hooks linked the bands to their respective load carriers. The increasing length of the bands was observed day by day through the closed glass doors of the

[1] Dietzel, Polytechnisches Centralblatt, 689–94 (1857); Fortschr. Phys. 143 (1857); Todhunter and Pearson, *History of the Theory of Elasticity*, Vol. II, Part I, 752.

[2] Kohlrausch, Ann. d. Physik **155**, 579 (1875); **158**, 337 (1876).

[3] Pulfrich, Ann. d. Physik **28**, 87 (1886).

[4] Bouasse and Carrière, Ann. de la Faculté des Sciences de Toulouse [5] **2**, 285 (1903).

[5] Phillips, Phil. Mag. **9**, 513 (1905).

[6] Schwartz, J. Inst. Elec. Eng. **44**, 693 (1910).

[7] Ariano, India Rubber J. **76**, 207 (1928); **78**, 316 (1929); Rubber Chem. and Tech. **3**, 62 (1930).

[8] Van Geel and Eymers, Zeits. f. physik. Chemie [3] **3**, 240 (1929); Rubber Age **29**, 9 (1929); Rubber Chem. and Tech. **2**, 545 (1929).

[9] Shacklock, Inst. Rubber Ind. Trans. **3**, 568 (1933).

cabinet by means of a meter scale. A plane mirror behind the pointers enabled observations to be made without parallax to tenths of millimeters. The specimens were shielded from strong light. They were subjected to room temperature fluctuations but readings in this experiment were taken only when the thermometer hanging with the bands showed 27.0°C (the temperature of the room being altered when necessary in order to attain this figure). Eleven of the specimens were number 50 two-inch stock bands furnished through the courtesy of the Goodrich Tire and Rubber Company, and "made from very high grade rubber gum, with the addition of only such ingredients as are necessary to produce a vulcanized rubber band of highest grade." These bands were approximately 1.5×1.5 mm in cross section and, when stretched by a 53 g tension between two pins to the extent that all slack was taken up, averaged about 5 cm in length. The remaining specimen was a ring about 1×4 mm in cross section and about 31.8 mm inside diameter made of pure gum vulcanized in a mold at the National Bureau of Standards.

The respective loads were placed on the hangers while the hangers were held in position with supporting fingers from beneath, the hand then being slowly lowered. Each specimen was given from 10 to 12 seconds during which to accept responsibility for the full magnitude of the load. This time element was provided in order to allow the bands to be stretched more or less isothermally. To obtain a reading of the length of the band at the instant of acceptance of the load was not always possible, but it was possible to obtain fairly reliable readings after 20 seconds from the beginning of the drop. The twelve bands were stressed as follows: 3 with 350 g, 4 (including the molded specimen) with 550 g, 3 with 750 g, and the remaining 2 with 1000 g. Triplicate loads were chosen in order to determine the significance of individual differences in specimens under the same factors.

TABLE I. *Breaking time in days for rubber bands under various constant loads at 27°C.*

Band Number	Original Length, l_0	Constant Load	Life in Days	Average Life
1	5.00 cm	350 g	252 da	
2	4.95	350	240	
3	5.20	350	228	240 da
4	4.95	550	195	
5	5.05	550	203	
6	4.80	550	228	209
7	5.15	550	115	
8	5.00	750	202	
9	5.10	750	203	
10	4.95	750	302	236
11	5.00	1000	315	
12	5.15	1000	228	271
Average	5.02		226	239
Median	5.00		228	238
Mode	5.00		228	

A dial hygrometer placed within the cabinet showed that, although relative humidity was not constant, as far as could be determined its normal variation had no effect upon the drift. The effect of temperature upon the length of the bands, however, was very marked. Observations on this effect will be dealt with in a separate paper. Cords, tubes, or strips of rubber doubtless would have provided specimens of more uniform cross section, but bands were chosen because of simplification of the grip problem.

RESULTS

Observations of the lengths of the bands at 27.0°C were made daily, or every few days, until the last band was found broken on the 316th day. The ring band (No. 7) had the shortest life, having broken on or about the 115th day. The life of the other bands ranged from 195 to 315 days as shown in Table I. It is interesting to note that the distribution of the lives of the 12 bands showed an average of 226, and both a median and a mode of 228 days. The latter statement is not altered by considering only the 11 similar bands, but the average life of the set is then increased 10 days. There seems to be no correlation between the load and the time that the specimen can support a given load.

By the term elongation in this experiment is meant the increase in length, e, beyond the original length, l_0, of the specimen. That is, with l representing the length of the band at a given time,

$$l=l_0+e.$$

The variation of the several elongations with time is shown in Figs. 1–3, which present graphs

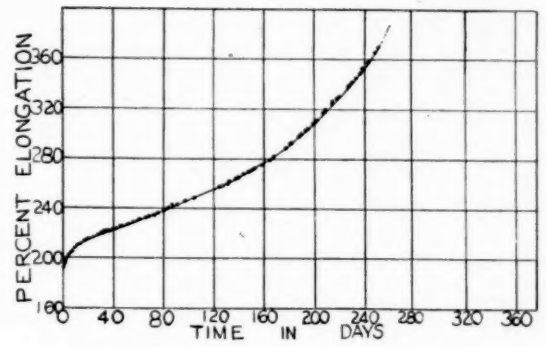

FIG. 1. 350 grams tension.

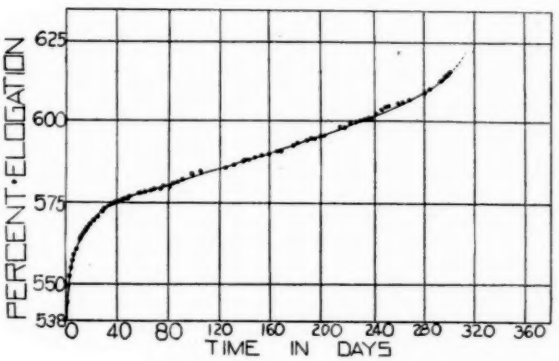

FIG. 2. 750 grams tension.

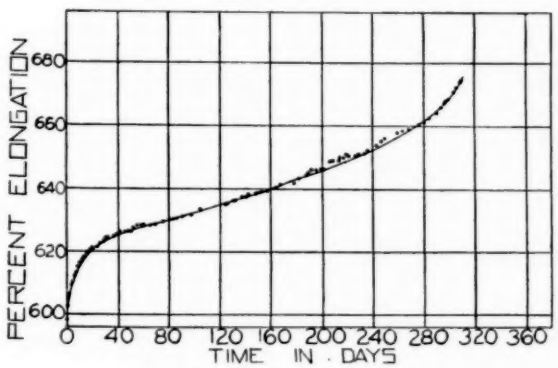

FIG. 3. 1000 grams tension.

FIGS. 1–3. Drift in rubber under constant tension at 27°C.

of representative specimens for each load. Curves for the other specimens were similar though not identical. These figures indicate that in each case the elongation of the band increased continually from the time of application of the load to the time of breaking of the band. The drift never ceased. In Table II the percent elongation for four representative bands is given for 16 arbitrarily chosen durations. In this table is also given an approximation of Young's modulus based on the cross section, a_0, of the unstretched specimen. The problem of the selection of specimens of uniform original cross section was not completely solved, and it is assumed that for this reason irregularities necessarily exist in the figures for the modulus as shown in Table II. If it is legitimate to use the phrase, Young's modulus, for a coefficient defined as the constant load in dynes multiplied by the ratio l_0/a_0 and divided by the variable e, then the modulus, M, itself, becomes, with e, a function of the time of drift. Templin and Sturm[10] seem to use it in this functional way. (Froman[11] discusses Young's modulus as a variable.)

Figs. 1–3 indicate not only that the drift effect was continuous, but also that its rate was neither constant nor uniform. For the rubber used in this experiment, the rate of drift began comparatively high, decreased to a minimum greater than zero, and then gradually but definitely increased until finally the band gave way. The inflection was so gradual that it might easily have been misinterpreted as a constant rate for some tens of days in the region centering roughly about the second or third month. As time went on, however, the increase in the rate became unmistakable. Table III presents, for different times, the magnitude of the rate of drift as determined by the tangent to the elongation curve at the respective time points. The minimum rate (that at the inflection point) was located at about 50, 110, 100, and 80 days, respectively, for the four specimens. There was thus no correlation between the load and the locus of the inflection point. The rate of drift in the vicinity of the breaking point is of course an accidental function, and statistically may be considerably higher than shown.

The positively accelerated portion of the drift may plausibly be explained by oxidation or other deterioration of the rubber. Not even for the smallest load, however, was the phenomenon of cracking or of any other change observable with a magnifying lens slowly moved along the stretched bands during the latter part of their lives. Furthermore, in no case did a specimen

[10] Templin and Sturm, Proc. A.S.T.M. [II] **31**, 882 (1931).
[11] Froman, Phys. Rev. **35**, 264 (1930).

TABLE II. *Drift in rubber bands as indicated (a) by time change in percent elongation, $E=(e/l_0)$ 100 and (b) by change in Young's modulus, $M=(F/a_0)/(e/l_0)$ in dynes per cm², at different time intervals under various constant loads at 27°C. $a_0=2(1.5\times1.5)$ mm².*

	Constant Load in Grams							
	350		550		750		1000	
Time Under Constant Stress	*E*	*M*	*E*	*M*	*E*	*M*	*E*	*M*
10 sec.	165	462×10^4	322	372×10^4	455	359×10^4	526	414×10^4
1 min.	170	448	329	364	475	344	547	397
10 min.	180	423	342	350	501	326	568	383
1 hr.	184	414	354	339	519	315	580	375
1 day	192	397	400	300	544	301	598	364
10	208	366	440	272	554	296	615	352
20	214	356	452	265	568	288	620	351
40	223	342	465	258	576	284	625	348
60	230	332	473	254	580	282	628	346
80	239	319	479	250	582	281	630	345
100	247	309	481	249	585	280	631	344
125	256	297	488	246	587	278	634	343
150	271	281	493	243	591	276	639	341
190	300	254	502	239	596	272	645	337
240	354	215	—	—	604	271	652	334
300	—	—	—	—	618	264	668	326
Break	371	205	515	233	619	264	680	320
Inflection	226	337	485	247	584	270	630	345
Breaking Time	252 da		228 da		302 da		315 da	
Inflection Time	50		110		100		80	
Band No.	1		6		10		11	
Unstressed Length, l_0	5.00 cm		4.80 cm		4.95 cm		5.00 cm	

break from a gradual tear. Each band seemed entirely homogeneous until the final snap, and the break usually occurred at a supporting hook rather than at a weld or other point of low resistance in the band. Should a plastization effect take place in rubber subjected to prolonged tension, it is quite thinkable that the line of drift may not merely curve upward during the latter days of the specimen, but that under suitable conditions it may eventually rise asymptotically as the breaking point is reached

PART II. EXPERIMENTAL

In order to investigate more thoroughly the early stages of the drift curve, the frame of a usual laboratory type of Hooke's law apparatus was used to support vertically a 1×65 cm glass tube, wound with 7 turns per cm of No. 27 Nichrome resistance wire, held co-axially in a 2 cm glass jacket to shield it from convection currents and from extraneous temperature gradients. In the inner bore there was suspended a specimen rubber band in such a manner that at its fully stretched length it was well within the constant temperature region of the chamber. A long mirror scale was placed vertically in juxtaposition with a pointer fastened to the wire which linked the specimen to its load. Readings were readily estimated to tenths of millimeters. Parallel with the specimen chamber there was a similarly constructed calibration or temperature observing chamber connected in the same electrical circuit as that of the specimen tube. The load was applied to the specimen manually with a 20 sec. interval for the drop. A reading of the length of the band was taken at the instant of acceptance of the full value of the load, and thereafter at variously dispersed intervals throughout the

TABLE III. *Rate of drift, $\Delta e/\Delta t_k$, in percent elongation per day at selected times for rubber bands under various constant loads at 27°C.*

Time Point, k	Constant Load in Grams			
	350	550	750	1000
5th day	1.44%/da	2.60	1.74	1.46
10th	0.95	1.64	0.94	0.93
20th	0.50	0.88	0.51	0.38
60th	0.39	0.31	0.13	0.12
100th	0.43	0.21	0.12	0.12
200th	0.99	0.31	0.15	0.15
Breaking Point	1.20	0.41	0.49	1.00
Minimum Rate	0.36	0.20	0.12	0.11

three week period of the strained life of the band. The specimen was a No. 14 gauge Goodrich band.

RESULTS

Fig. 4 is a graph of the data taken in the second part of the experiment. A 6.12 cm band was subjected to a constant load of 300 g at 40°C. (The temperature varied a few degrees from this figure during the course of the experiment, but all readings were taken at 40°C.) The drift curve was plotted to each of three different time scales, *viz.*, seconds, minutes and hours. Although the graph seemed quite uniform and consistent, it appeared upon analysis that its mathematical expression required two distinct functions, one a logarithmic function governing the early portion of the curve, say between 30 and 5000 seconds from the time of acceptance of the load, and the other a power law covering the whole drift effect from about the 80th minute to the breaking point which occurred on the twentieth day, before a drift inflection could take place. These two empirical functions are, for the respective early and latter time periods,

$$l = l_0 + e_0 + e_t$$
$$= 6.12 + 17.52 + 0.84 \log t \quad 30 < t < 7000 \text{ sec.} \quad (1)$$
$$= 6.12 + 17.88 + 2.66 t^{0.195} \quad 1 < t < 500 \text{ hr.} \quad (2)$$

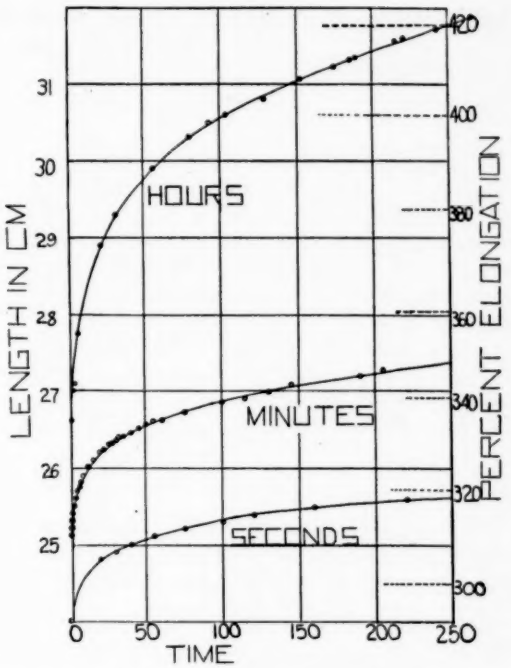

FIG. 4. Drift in rubber under constant tension of 300 g at 40°C. $L = 23.64 + 0.84 \log t$ where $30 < t < 7000$ seconds. $L = 24.00 + 2.66\ t^{0.195}$, where $1 < t < 500$ hours.

where l is the length in cm of the specimen at time t, l_0 its original unstretched length, e_0 the elongation in cm produced by the application of the load, e_t the drift or additional elongation in cm at time t, and where t is the time measured from the moment of acceptance of the full load by the band. In Eq. (1) t is measured in seconds while in (2) it is measured in hours.

The very nature of the log law indicates that it of itself cannot be a complete expression for the phenomenon. Yet it is interesting to note that when used for the beginning of the curve, the average deviation for the 30 readings between 30 and 6000 seconds is only ± 0.016 cm. The average deviation from the power law for the 94 observations between 1 and 500 hours is ± 0.045 cm. These deviations are well within experimental error in the taking of the observations.

The Double Mobility of Some Non-Newtonian Fluids with Particular Reference to Cellulose Nitrate Sols

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(Received July 1, 1936)

The ratio of the mobility of nitrocellulose solutions at high shearing stresses to the mobility at low shearing stresses, where there exists in fact true fluidity, is called the "mobility ratio." This mobility ratio may be very high for certain "medium" and "high viscosity" nitrocottons, but it does not necessarily prove to be a figure proportional to the usually accepted "viscosity." Thus mixtures of "high" and "low" viscosity nitrocottons may be so blended that, although showing similar low shearing stress viscosities with the falling ball, one will show at high shearing stresses much higher viscosity than the other. Certain "low" viscosity nitrocottons appear to show a nearly constant true viscosity at all rates of shear. The two mobilities show significant differences in technical behavior. Thus under given conditions of use, such as spraying, brushing, roller coating, etc., the high stress mobility determines what may be called the *solvent demand* of the sol, whereas the viscosity at low stresses indicates the characteristics to be expected after application.

ONE of the most important designations of commercial cellulose nitrates is the viscosity of a sol of a given concentration. With the possible exception of the relegation of cellulose nitrates into the two groups of acetone-soluble and alcohol-soluble esters, the lacquer, leather cloth, etc., manufacturers employ the criterion of viscosity of the sols as a determinant of those technically important qualities of solvent demand, intrinsic strength of film, etc., as reference to the cellulose nitrate manufacturers' trade literature will indicate.

The viscosities of the sols are usually determined in the trade by the falling sphere method, and are expressed for given concentrations of nitrocotton in acetone or other dispersing agent in absolute units of viscosity or the equivalent as a time of fall of a standard steel ball under given conditions in apparatus of standardized dimensions. The use of the physical property indicating the internal resistance to flow of the sol as a viscosity under unspecified conditions of stress or velocity gradient thus renders it evident that such products have been tacitly assumed to be *true* fluids.

TABLE I. *Comparison of "viscosities" of 7.5 percent sols of two cellulose nitrates in butyl acetate.*

Radius of ball cm	No. 1	No. 2
0.397	116	37.0
0.355	121	38.0
0.316	136	38.1
0.277	156	40.9(?)
0.237	172	39.0
0.197	190	38.9
0.158	215	38.4
0.119	248	39.3
0.077	317	39.1

This is indeed not the case, cellulose nitrate and possibly all cellulose ester sols being non-Newtonian fluids. Such fluids are defined as those showing an internal resistance to shear which varies with the stress applied although outwardly conforming to true fluids in being free from rigidity ("yield value"). This fact being, however, not unknown to rheologists, it is the purpose of this communication to show that cellulose nitrate and indeed other non-Newtonian fluids examined by the authors can be designated in their physical or rather their dynamic properties by *two mobilities*, the one characteristic of shear at very low stresses and the other at high stresses. When we consider for the moment the commonly used method of the falling sphere for determining the viscosity of cellulose nitrate sols, it is evident that if this constant is not independent of the rate of shear during its determination, a change in the rate of shear (radius or specific gravity of ball) should influence the value of viscosity obtained. In Table I are shown the viscosities obtained by the employment of varying sizes of steel balls on two sols of cellulose nitrate of different origin. The viscosities in Table I were calculated from the times of fall by application of the Francis'[1] correction to Stokes' original formula:

$$\eta = \frac{2}{9}\frac{gr^2(D-d)t(1-r/R)^{2.25}}{S},$$

[1] A. W. Francis, Physics **4**, 405 (1933).

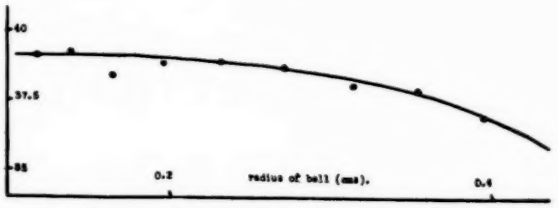

FIG. 1. No. 45 cellulose nitrate. 7.5 percent sol in mixed solvents. Apparent viscosity (falling sphere, Francis' correction) against radius of steel balls.

where D, d refer to densities of ball and fluid, respectively, and r and R to the radii of the sphere and containing cylinder. S = height of fall. As will be seen, although virtual constancy is obtained in the less viscous sol over the range of rates of fall examined, "viscosities" steadily fall in the other case with increase in the radii of the balls.

That the constancy of viscosity with increasing rate of shear is not necessarily characteristic of a given sol is shown in Fig. 1 wherein it is seen that when the rate of fall of the ball is sufficiently high, constancy of viscosity gives way to a diminution with the rate of shear. Change of viscosity with rate of shear being thus indicated, the possibility of a limiting value of mobility at high shearing stresses by means of a plastometer capable of the application of stresses up to 40,000 dynes was next considered.

The results of the plastometer shear of cellulose nitrate sols with curvilinear shear/efflux relationships have already been the subject of a considerable number of publications. There arise, however, two important points in connection with such results which need to be considered before any conclusions can be drawn. In the first place, in attempts to explore high regions of shear, the kinetic energy effect may be considerable and in the absence of any very definite information as to its correction in the case of non-Newtonian materials, it is preferable to so choose the dimensions of the capillary that its effect is negligible or below the limit of the accuracy of interpretation of results. This is secured by ensuring that the ratio of pressure lost in kinetic energy manifestation to total pressure is below 0.1 percent or that

$$Q^2/P \gg (\pi^2 R^4 g\rho)/1000.$$

The second point concerns the interpretation of

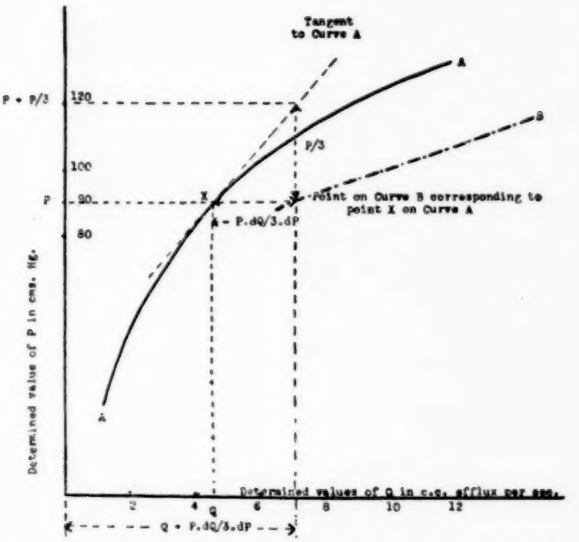

FIG. 2. Illustrated example of method of determining P/vel. grad. $\times K$ curve from P/Q values from plastometric data.

results. In a publication by M. Mooney,[2] it was pointed out that by a treatment of stress/shear data due to Rabinowitsch, the characterization of stress/shear data could be possible only if and when the "viscosity" returned coincided dimensionally with the stress per unit velocity gradient. The formulation of a true value for velocity gradient, which in the case of non-Newtonian fluids and plastics is *not* proportional to the velocity of efflux, was obtained by a treatment in which no assumption as to the constancy of viscosity, or its reciprocal, fluidity, was made, the fluidity term being integrated with the known variable of stress at the capillary wall. The derivation may perhaps be still more simply shown by employing terms in which no characteristic related to fluidity or viscosity appears:

Since $s = Pr/2l$ and $S = pR/2l$,

where s = stress at any radius r within the capillary, S = stress at the capillary wall of radius R, $s/S = r/R$; $r = Rs/S$; $dr = Rds/S$.

The efflux velocity $Q = \int_0^R \pi r^2 V' dr$,

where V' = velocity gradient

$$Q = (R/S)^3 \cdot \int_s^S \pi \cdot S^2 \cdot V' \cdot ds,$$

[2] M. Mooney, J. Rheology **2**, 210 (1931).

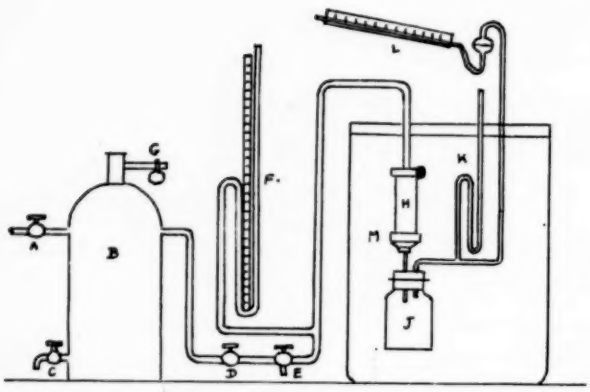

FIG. 3. Diagram of plastometer.

from which $3S^2Q+S^3dQ/dS=\pi\cdot R^3S^2V'$ and

$$V'=(3Q+S\cdot dQ/dS)/\pi\cdot R^3. \qquad (1)$$

Whereas viscosity and fluidity, considered as defined constants, can have no place in non-Newtonian fluids or plastic bodies, mobility μ or d(velocity gradient)/d(stress) may serve to characterize materials in which the vel. gradient/stress relationship does not extrapolate to the origin.

The plotting of results accruing from variable pressure capillary shear is rendered very simple indeed if graphical means be used to obtain the derived curve from the pressure/volume velocity graph. Eq. (1) may be written in the form:

$$V'\times K=Q+P\cdot dQ/3\cdot dP, \qquad (2)$$

where P = pressure in cm of mercury. In Fig. 2 is shown (curve A) the usual curvilinear P/Q relationship obtained by the capillary shear of any non-Newtonian fluid, and the legend shows how curve B is obtained therefrom. In practice, values of P conveniently divisible by 3 are selected and corresponding values of $Q+PdQ/3dP$, found on the tangent to the point P where the tangent cuts the $P+P/3$ line horizontally, are brought vertically down to the P ordinate, the tangents being laid off by means of a celluloid ruler. The line B, when completed, will then be a *measure* of the relationship between the stress and velocity gradient, although coefficients are necessary for conversion to absolute units. Over the range where this curve B assumes linearity, although not extrapolating to the origin, a constant mobility is shown when the nondimensional relationship $d(Q+P\cdot dQ/3\cdot dP)/dP$ is converted to a dimensional mobility

$$d(3\cdot Q+S\cdot dQ/dS)/d(S\cdot\pi\cdot R^3)$$

by multiplication with the necessary instrumental constants.

$$S=(Hg\rho R)/2L,$$

where H = cm of mercury; $g=981$; $\rho=13.6$, the other terms having their usual significance.

The foregoing treatment has the advantage of requiring far less labor than would be involved by the algebraic calculation of differential coefficients at each determined point and the plotting of the ordinates in absolute units. No disadvantages arise since only one relationship in absolute units, *viz.* the mobility, is desired, which can only usefully be obtained from a point on the linear portion of the curve.

It will be shown in the following that when the results of capillary shear from non-Newtonian fluids, including cellulose nitrate sols at sufficiently high rates of shear, are plotted, constant shear/velocity gradient relationships *are* obtained, when the error caused by the kinetic energy effect is avoided by suitable apparatus. The plastometer used was that originally described in an earlier publication[3] and comprises as an essential the continuous reading flowmeter included therewith.[4] For measurement of velocities of efflux at very low rates of shear (corresponding to velocity gradients even lower than can be obtained with the smallest of falling spheres), a simple modification of the flowmeter is used. This merely involves connecting the displaced air outlet from the receiver bottle to a long calibrated glass tube and allowing the displaced air to entrain a soap bubble, the rate of linear travel of which is measured and calculated by calibration to cm³ of efflux per second. By this means velocities of efflux as low as desired may be obtained.

It is more convenient thus to employ the

[3] de Waele, J. Oil and Colour Chemists' Assoc. **6**, 33 (1923).

[4] Since this publication is not easily available, illustrations and brief descriptive matter relating to the apparatus are given here. Fig. 3 shows a conventional diagram of the apparatus comprising compressed air inlet A, compressed air reservoir B, drain cock C, D and E control valves for entry and release of compressed air, F the mercury manometer, G safety valve, H plastometer container adapted to hold lead color tube, J the receiver jar, leading to air-lead K and 1/10 flowmeter L.

plastometer for the purpose of determining the shear behavior of both high and low stress extrusions, but the measurement of the latter then necessitates a change from a "fast" to a "slow" capillary, i.e., to one in which the pressure/efflux velocity ratio is of a high order in order to avoid the errors in making very low manostatic measurements.[5]

In Figs. 4 and 5 are shown typical graphs of two cellulose nitrate sols of different origins, both materials being dispersed in a mixed solvent consisting of equal parts by weight of ethyl acetate, ethyl alcohol and butyl acetate. In both cases curve A represents the plotting of shearing pressures (cm mercury) against velocity of efflux, curve B being the derived plot of pressure against $V' \times k$. Although the two axes have been scaled in dimensional shearing stresses and velocity gradients, these scales only apply to curves B. Curves C represent the stress/velocity-gradient line correctly scaled and derived from

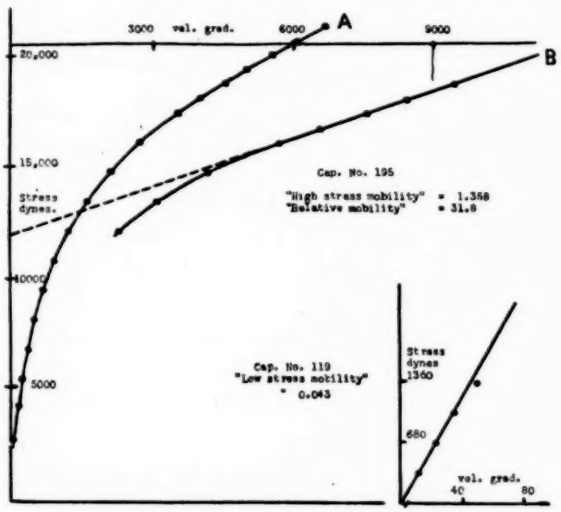

FIG. 4. No. 8 cellulose nitrate 7.5 percent sol in mixed solvents.

[5] In Figs. 4 and 5, the B curves derived from the corresponding A curves by the graphical method referred to, have been set correctly to S/V' (or true dimensional) values by introduction of absolute unit scales on the axes. It is to be noted that the scaling does not apply to the A curves.

In the low stress graphs, since the only point used to evaluate the "low stress" μ lies on a straight line to the origin where $V'/S = dV'/dS$, the A curve values only have been plotted, since the sole useful point necessary to derive μ is that where the curve is characteristic of a true fluid, i.e., linear and extrapolating to the origin. In such cases it is obvious that

$$4Q/\pi R^3 = (3Q + S \cdot dQ/dS)/\pi R^3.$$

the low stress extrusions referred to previously. It will be seen that while linearity at upper values of the higher stresses is shown in both figures, some linearity and extrapolation to the origin obtains only with the low stress extrusions in the case of Fig. 4, that in Fig. 5 shows apparently continuous curvature. A close approximation to the mobility obtaining at zero stress is however obtainable without difficulty in these cases.

At any points on the S/V' curve, mobilities dV'/dS may be graphically calculated, whether they be variable or constant. In Fig. 6 are shown the plottings of μ against stresses for four 7.5 percent cellulose nitrate sols of differing origins but dispersed in the same solvents as above mentioned. The curves show the linking up of the high stress (fast capillary) to the low stress results and although on a scale not permitting one to recognize constancy of μ (where existent) towards the origin, they clearly show this at the upper values.

In Fig. 7, the "distribution curves" showing $d\mu/dS$ plotted against S indicate clearly amongst other points, a close similarity between two pairs of colloids insofar as the attainment of a constant upper mobility is a characteristic of the material.

In Table II are summarized the characteristics of the four cellulose nitrates obtained from the data shown in the figures.

It is clearly to be seen from Table II that the relative mobility, a figure which definitely measures divergence of the sol from the condi-

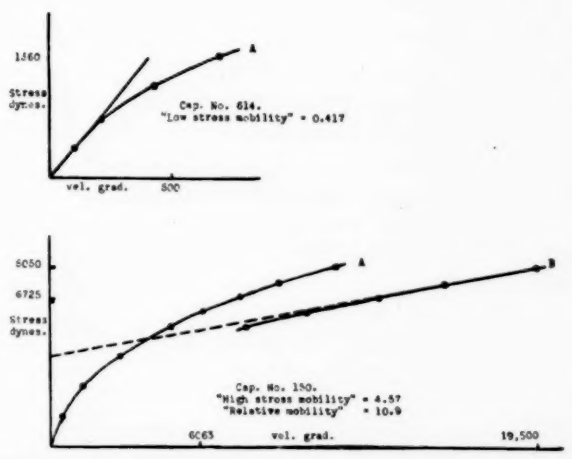

FIG. 5. No. 5 cellulose nitrate 4 percent sol in mixed solvents.

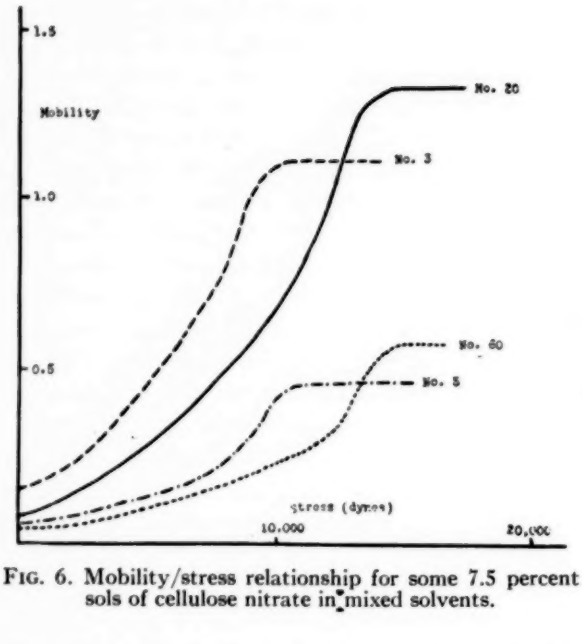

FIG. 6. Mobility/stress relationship for some 7.5 percent sols of cellulose nitrate in mixed solvents.

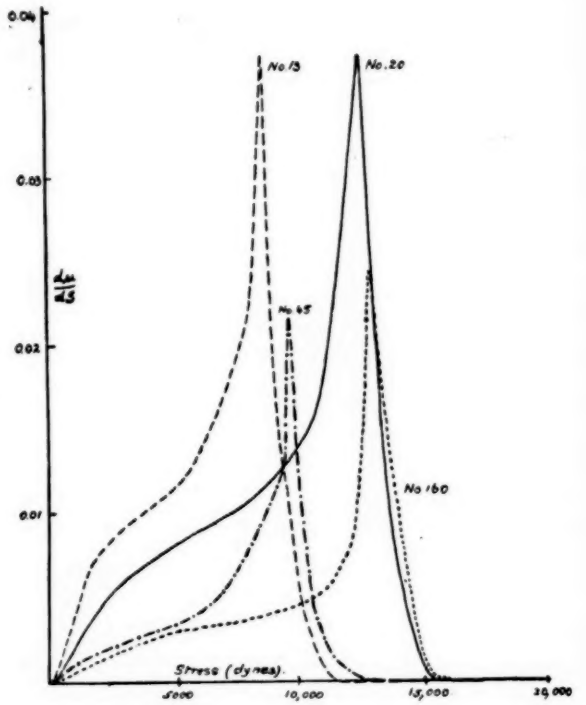

FIG. 7. 7.5 percent cellulose nitrate sols in mixed solvents. Rate of change of mobility/stress against stress.

tion of molecular dispersion is unconnected with its generally accepted viscosity (low stress viscosity). This point is interesting in view of the suggestion often made that viscosity is indicative of the condition of colloidal dispersity.

In Fig. 8 are shown the results of the plotting of some of the same constants against concentration, the sol in this case being from another cotton dispersed in butyl acetate only. The lines shown are merely interesting in indicating that the "critical stress" is characteristic only of the concentration, the nature of the mobility/concentration curves precluding any attempt at useful extrapolation.

Fig. 9 shows a pair of S/V' curves from the high and low stress shear respectively of a 7.5 percent cellulose nitrate of the low viscosity type used in lacquer manufacture, the solvent being again the mixed one. The curves nearly simulate those of true fluids, the similarity being clearly indicated by the closeness of the relative mobility (1.1) to that of a true fluid.

In Table III are shown some flow characteristics of other non-Newtonian fluids. The significance of the double mobility of the non-Newtonian fluids described demands a consideration which the writers do not feel competent to undertake, especially since the work described was concluded comparatively recently. In re erence to cellulose nitrate sols considered as media for coating, spraying, etc., it may, however, be

TABLE II. *Characteristics of four 7.5 percent cellulose nitrate sols in mixed solvents.*

No.	Mobility		Relative Mobility col. (2) ÷ col. (3)	Critical Stress (dynes) where upper μ is constant
	High Stress	Low Stress		
5	0.474	0.055	8.6	12,770
3	1.130	0.161	7.0	11,410
20	1.350	0.073	18.4	15,450
60	0.590	0.0435	13.5	15,450

TABLE III. *Flow characteristics of some non-Newtonian fluids.*

Sol	Mobility		Relative Mobility
	High Stress	Low Stress	
20% masticated rubber in toluene	0.286	0.052	5.5
60% crepe rubber in mineral oil	0.026	0.016	1.6
40% Gum arabic in water	0.0767	0.0598	1.28

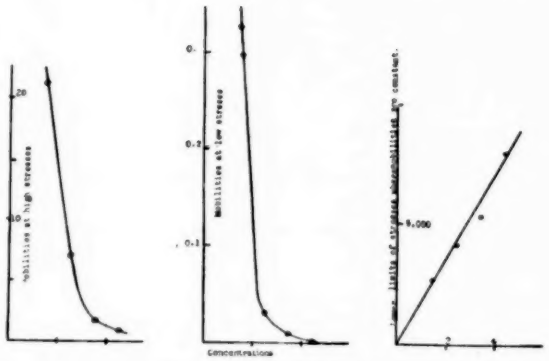

FIG. 8. Some characteristics of No. 40 cellulose nitrate in butyl acetate at varying concentrations.

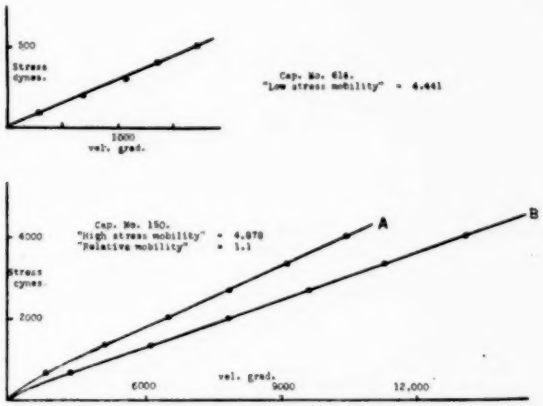

FIG. 9. No. 5A cellulose nitrate ("low viscosity"), 7.5 percent sol in mixed solvents.

suggested that in technical practice, while low stress mobility may undoubtedly govern solvent demand so far as dispersion to a sol is concerned, the higher rates of shear obtaining under working conditions may strongly influence the application of the coating. Evaluation of the higher stress mobilities, may lead to an explanation of those anomalies of coating performance shown by two lacquers of apparently similar properties as judged by the usual criteria of low stress mobility.